



(12) **United States Patent**
Chen et al.

(10) **Patent No.:** **US 9,111,877 B2**
(45) **Date of Patent:** **Aug. 18, 2015**

(54) **NON-LOCAL PLASMA OXIDE ETCH**

(71) Applicant: **Applied Materials, Inc.**, Santa Clara, CA (US)
(72) Inventors: **Zhijun Chen**, Milpitas, CA (US); **Seung Park**, San Jose, CA (US); **Mikhail Korolik**, San Jose, CA (US); **Anchuan Wang**, San Jose, CA (US); **Nitin K. Ingle**, San Jose, CA (US)

(73) Assignee: **Applied Materials, Inc.**, Santa Clara, CA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 340 days.

(21) Appl. No.: **13/790,668**

(22) Filed: **Mar. 8, 2013**

(65) **Prior Publication Data**
US 2014/0166617 A1 Jun. 19, 2014

Related U.S. Application Data

(60) Provisional application No. 61/738,855, filed on Dec. 18, 2012.

(51) **Int. Cl.**
H01L 21/302 (2006.01)
H01L 21/311 (2006.01)
H01J 37/32 (2006.01)

(52) **U.S. Cl.**
CPC **H01L 21/31122** (2013.01); **H01J 37/3244** (2013.01); **H01J 37/32357** (2013.01); **H01J 37/32422** (2013.01)

(58) **Field of Classification Search**
None
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

2,369,620 A	2/1945	Sullivan et al.
3,451,840 A	6/1969	Hough
3,937,857 A	2/1976	Brummett et al.
4,006,047 A	2/1977	Brummett et al.
4,209,357 A	6/1980	Gorin et al.

(Continued)

FOREIGN PATENT DOCUMENTS

CN	1375575	10/2002
CN	1412861 A	4/2003

(Continued)

OTHER PUBLICATIONS

Norasetthekul, S. et al "Dry etch chemistries for TiO₂ thin films" Applied Surface Science 2001, 185 (1-2) 27-33.*

(Continued)

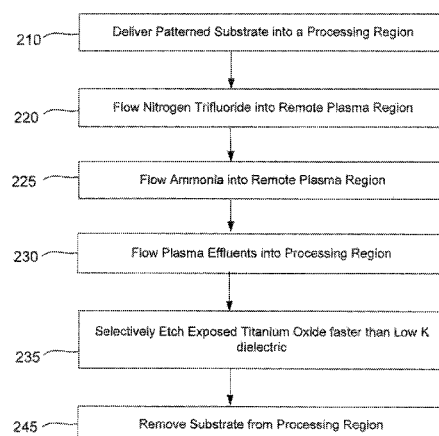
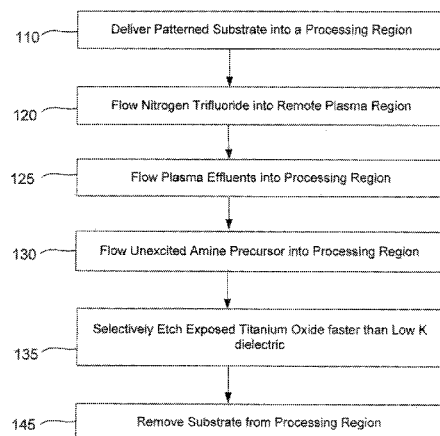
Primary Examiner — Anita Alanko

(74) *Attorney, Agent, or Firm* — Kilpatrick Townsend & Stockton LLP

(57) **ABSTRACT**

A method of etching exposed titanium oxide on heterogeneous structures is described and includes a remote plasma etch formed from a fluorine-containing precursor. Plasma effluents from the remote plasma are flowed into a substrate processing region where the plasma effluents may combine with a nitrogen-containing precursor such as an amine (N:) containing precursor. Reactants thereby produced etch, the patterned heterogeneous structures with high titanium oxide selectivity while the substrate is at elevated temperature. Titanium oxide etch may alternatively involve supplying a fluorine-containing precursor and a source of nitrogen-and-hydrogen-containing precursor to the remote plasma. The methods may be used to remove titanium oxide while removing little or no low-K dielectric, polysilicon, silicon nitride or titanium nitride.

20 Claims, 5 Drawing Sheets



(56)

References Cited

U.S. PATENT DOCUMENTS

4,214,946	A	7/1980	Forget et al.	5,403,434	A	4/1995	Moslehi
4,232,060	A	11/1980	Mallory et al.	5,413,967	A	5/1995	Matsuda et al.
4,234,628	A	11/1980	DuRose	5,415,890	A	5/1995	Kloiber et al.
4,265,943	A	5/1981	Goldstein et al.	5,416,048	A	5/1995	Blalock et al.
4,364,803	A	12/1982	Nidola et al.	5,420,075	A	5/1995	Homma et al.
4,368,223	A	1/1983	Kobayashi et al.	5,429,995	A	7/1995	Nishiyama et al.
4,397,812	A	8/1983	Mallory, Jr.	5,439,553	A	8/1995	Grant et al.
4,468,413	A	8/1984	Bachmann	5,451,259	A	9/1995	Krogh
4,565,601	A	1/1986	Kakehi et al.	5,468,342	A	11/1995	Nulty et al.
4,571,819	A	2/1986	Rogers et al.	5,474,589	A	12/1995	Ohga et al.
4,579,618	A	4/1986	Celestino et al.	5,478,462	A	12/1995	Walsh
4,585,920	A	4/1986	Hoog et al.	5,483,920	A	1/1996	Pryor
4,632,857	A	12/1986	Mallory, Jr.	5,500,249	A	3/1996	Telford et al.
4,656,052	A	4/1987	Satou et al.	5,505,816	A	4/1996	Barnes et al.
4,690,746	A	9/1987	McInerney et al.	5,510,216	A	4/1996	Calabrese et al.
4,714,520	A	12/1987	Gwozdz	5,516,367	A	5/1996	Lei et al.
4,749,440	A	6/1988	Blackwood et al.	5,531,835	A	7/1996	Fodor et al.
4,753,898	A	6/1988	Parrillo et al.	5,534,070	A	7/1996	Okamura et al.
4,807,016	A	2/1989	Douglas	5,536,360	A	7/1996	Nguyen et al.
4,810,520	A	3/1989	Wu	5,549,780	A	8/1996	Koinuma et al.
4,816,638	A	3/1989	Ukai et al.	5,558,717	A	9/1996	Zhao et al.
4,851,370	A	7/1989	Doklan et al.	5,560,779	A	10/1996	Knowles et al.
4,865,685	A	9/1989	Palmour	5,563,105	A	10/1996	Dobuzinsky et al.
4,872,947	A	10/1989	Wang et al.	5,571,576	A	11/1996	Qian et al.
4,886,570	A	12/1989	Davis et al.	5,578,130	A	11/1996	Hayashi et al.
4,892,753	A	1/1990	Wang et al.	5,591,269	A	1/1997	Arami et al.
4,894,352	A	1/1990	Lane et al.	5,599,740	A	2/1997	Jang et al.
4,904,341	A	2/1990	Blaugher et al.	5,624,582	A	4/1997	Cain
4,951,601	A	8/1990	Maydan et al.	5,626,922	A	5/1997	Miyanaga et al.
4,960,488	A	10/1990	Law et al.	5,645,645	A	7/1997	Zhang et al.
4,981,551	A	1/1991	Palmour	5,648,125	A	7/1997	Cane
4,985,372	A	1/1991	Narita et al.	5,648,175	A	7/1997	Russell et al.
4,994,404	A	2/1991	Sheng et al.	5,656,093	A	8/1997	Burkhart et al.
5,000,113	A	3/1991	Wang et al.	5,661,093	A	8/1997	Ravi et al.
5,013,691	A	5/1991	Lory et al.	5,674,787	A	10/1997	Zhao et al.
5,030,319	A	7/1991	Nishino et al.	5,679,606	A	10/1997	Wang et al.
5,061,838	A	10/1991	Lane et al.	5,695,810	A	12/1997	Dubin et al.
5,089,441	A	2/1992	Moslehi	5,712,185	A	1/1998	Tsai et al.
5,089,442	A	2/1992	Olmer	5,716,500	A	2/1998	Bardos et al.
5,147,692	A	9/1992	Bengston	5,716,506	A	2/1998	Maclay et al.
5,156,881	A	10/1992	Okano et al.	5,719,085	A	2/1998	Moon et al.
5,186,718	A	2/1993	Tepman et al.	5,733,816	A	3/1998	Iyer et al.
5,198,034	A	3/1993	deBoer et al.	5,747,373	A	5/1998	Yu
5,203,911	A	4/1993	Sricharoenchalkit et al.	5,755,859	A	5/1998	Brusic et al.
5,215,787	A	6/1993	Homma	5,756,402	A	5/1998	Jimbo et al.
5,228,501	A	7/1993	Tepman et al.	5,781,693	A	7/1998	Ballance et al.
5,231,690	A	7/1993	Soma et al.	5,786,276	A	7/1998	Brooks et al.
5,235,139	A	8/1993	Bengston et al.	5,789,300	A	8/1998	Fulford
5,238,499	A	8/1993	van de Ven et al.	5,800,686	A	9/1998	Littau et al.
5,240,497	A	8/1993	Shacham et al.	5,804,259	A	9/1998	Robles
5,248,527	A	9/1993	Uchida et al.	5,812,403	A	9/1998	Fong et al.
5,252,178	A	10/1993	Moslehi	5,820,723	A	10/1998	Benjamin et al.
5,270,125	A	12/1993	America et al.	5,824,599	A	10/1998	Schacham-Diamand et al.
5,271,972	A	12/1993	Kwok et al.	5,830,805	A	11/1998	Shacham-Diamand et al.
5,275,977	A	1/1994	Otsubo et al.	5,838,055	A	11/1998	Kleinhenz et al.
5,279,865	A	1/1994	Chebi et al.	5,843,538	A	12/1998	Ehrsam et al.
5,288,518	A	2/1994	Homma	5,844,195	A	12/1998	Fairbairn et al.
5,290,382	A	3/1994	Zarowin et al.	5,846,332	A	12/1998	Zhao et al.
5,302,233	A	4/1994	Kim et al.	5,846,375	A	12/1998	Gilchrist et al.
5,306,530	A	4/1994	Stronglin et al.	5,846,598	A	12/1998	Semkow et al.
5,314,724	A	5/1994	Tsukune et al.	5,849,639	A	12/1998	Molloy et al.
5,316,804	A	5/1994	Tomikawa et al.	5,850,105	A	12/1998	Dawson et al.
5,319,247	A	6/1994	Matsuura	5,855,681	A	1/1999	Maydan et al.
5,328,558	A	7/1994	Kawamura et al.	5,856,240	A	1/1999	Sinha et al.
5,328,810	A	7/1994	Lowrey et al.	5,858,876	A	1/1999	Chew
5,334,552	A	8/1994	Homma	5,872,052	A	2/1999	Iyer
5,345,999	A	9/1994	Hosokawa	5,872,058	A	2/1999	Van Cleemput et al.
5,352,636	A	10/1994	Beinglass	5,882,786	A	3/1999	Nassau et al.
5,362,526	A	11/1994	Wang et al.	5,885,404	A	3/1999	Kim et al.
5,368,897	A	11/1994	Kurihara et al.	5,885,749	A	3/1999	Huggins et al.
5,380,560	A	1/1995	Kaja et al.	5,888,906	A	3/1999	Sandhu et al.
5,382,311	A	1/1995	Ishikawa et al.	5,891,349	A	4/1999	Tobe et al.
5,384,284	A	1/1995	Doan et al.	5,891,513	A	4/1999	Dubin et al.
5,385,763	A	1/1995	Okana et al.	5,897,751	A	4/1999	Makowiecki
5,399,529	A	3/1995	Homma	5,899,752	A	5/1999	Hey et al.
				5,904,827	A	5/1999	Reynolds
				5,907,790	A	5/1999	Kellam
				5,910,340	A	6/1999	Uchida et al.
				5,913,140	A	6/1999	Roche et al.

(56)

References Cited

U.S. PATENT DOCUMENTS

5,913,147 A	6/1999	Dubin et al.	6,197,680 B1	3/2001	Lin et al.
5,915,190 A	6/1999	Pirkle	6,197,688 B1	3/2001	Simpson
5,920,792 A	7/1999	Lin	6,197,705 B1	3/2001	Vassiliev
5,932,077 A	8/1999	Reynolds	6,203,863 B1	3/2001	Liu et al.
5,933,757 A	8/1999	Yoshikawa et al.	6,204,200 B1	3/2001	Shieh et al.
5,935,334 A	8/1999	Fong et al.	6,217,658 B1	4/2001	Orczyk et al.
5,937,323 A	8/1999	Orczyk et al.	6,228,233 B1	5/2001	Lakshmikanthan et al.
5,939,831 A	8/1999	Fong et al.	6,228,751 B1	5/2001	Yamazaki et al.
5,942,075 A	8/1999	Nagahata et al.	6,228,758 B1	5/2001	Pellerin et al.
5,944,902 A	8/1999	Redeker et al.	6,235,643 B1	5/2001	Mui et al.
5,951,601 A	9/1999	Lesinski et al.	6,238,513 B1	5/2001	Arnold et al.
5,951,776 A	9/1999	Selyutin et al.	6,238,582 B1	5/2001	Williams et al.
5,953,635 A	9/1999	Andideh	6,241,845 B1	6/2001	Gadgil et al.
5,968,610 A	10/1999	Liu et al.	6,242,349 B1	6/2001	Nogami et al.
5,969,422 A	10/1999	Ting et al.	6,245,670 B1	6/2001	Cheung et al.
5,976,327 A	11/1999	Tanaka	6,251,236 B1	6/2001	Stevens
5,990,000 A	11/1999	Hong et al.	6,251,802 B1	6/2001	Moore et al.
5,990,013 A	11/1999	Berenguer et al.	6,258,220 B1	7/2001	Dordi et al.
5,993,916 A	11/1999	Zhao et al.	6,258,223 B1	7/2001	Cheung et al.
6,010,962 A	1/2000	Liu et al.	6,258,270 B1	7/2001	Hilgendorff et al.
6,013,191 A	1/2000	Nasser-Faili et al.	6,261,637 B1	7/2001	Oberle
6,013,584 A	1/2000	M'Saad	6,277,752 B1	8/2001	Chen
6,015,724 A	1/2000	Yamazaki et al.	6,291,348 B1	9/2001	Lopatin et al.
6,015,747 A	1/2000	Lopatin et al.	6,312,995 B1	11/2001	Yu
6,020,271 A	2/2000	Yanagida	6,313,035 B1	11/2001	Sandhu et al.
6,030,666 A	2/2000	Lam et al.	6,319,387 B1	11/2001	Krishnamoorthy et al.
6,030,881 A	2/2000	Papasouliotis et al.	6,323,128 B1	11/2001	Sambucetti et al.
6,035,101 A	3/2000	Sajoto et al.	6,335,261 B1	1/2002	Natzle et al.
6,037,018 A	3/2000	Jang et al.	6,335,288 B1	1/2002	Kwan et al.
6,037,266 A	3/2000	Tao et al.	6,340,435 B1	1/2002	Bjorkman et al.
6,039,851 A	3/2000	Iyer	6,342,733 B1	1/2002	Hu et al.
6,053,982 A	4/2000	Halpin et al.	6,344,410 B1	2/2002	Lopatin et al.
6,059,643 A	5/2000	Hu et al.	6,350,320 B1	2/2002	Sherstinsky et al.
6,063,683 A	5/2000	Wu et al.	6,351,013 B1	2/2002	Luning et al.
6,063,712 A	5/2000	Gilton et al.	6,364,949 B1	4/2002	Or et al.
6,065,424 A	5/2000	Shacham-Diamand et al.	6,364,954 B2	4/2002	Umotoy et al.
6,072,227 A	6/2000	Yau et al.	6,364,957 B1	4/2002	Schneider et al.
6,077,780 A	6/2000	Dubin	6,372,657 B1	4/2002	Hineman et al.
6,080,529 A	6/2000	Ye et al.	6,375,748 B1	4/2002	Yudovsky et al.
6,083,344 A	7/2000	Hanawa et al.	6,379,575 B1	4/2002	Yin et al.
6,086,677 A	7/2000	Umotoy et al.	6,383,951 B1	5/2002	Li
6,087,278 A	7/2000	Kim et al.	6,387,207 B1	5/2002	Janakiraman et al.
6,093,594 A	7/2000	Yeap et al.	6,395,150 B1	5/2002	Van Cleemput et al.
6,099,697 A	8/2000	Hausmann	6,403,491 B1	6/2002	Liu et al.
6,107,199 A	8/2000	Allen et al.	6,416,647 B1	7/2002	Dordi et al.
6,110,530 A	8/2000	Chen et al.	6,432,819 B1	8/2002	Pavate et al.
6,110,836 A	8/2000	Cohen et al.	6,436,816 B1	8/2002	Lee et al.
6,113,771 A	9/2000	Landau et al.	6,440,863 B1	8/2002	Tsai et al.
6,117,245 A	9/2000	Mandrekar et al.	6,441,492 B1	8/2002	Cunningham
6,136,163 A	10/2000	Cheung et al.	6,446,572 B1	9/2002	Brcka
6,136,685 A	10/2000	Narwankar et al.	6,448,537 B1	9/2002	Nering
6,136,693 A	10/2000	Chan et al.	6,462,371 B1	10/2002	Weimer et al.
6,140,234 A	10/2000	Uzoh et al.	6,465,366 B1	10/2002	Nemani et al.
6,144,099 A	11/2000	Lopatin et al.	6,477,980 B1	11/2002	White et al.
6,147,009 A	11/2000	Grill et al.	6,479,373 B2	11/2002	Dreybrodt et al.
6,149,828 A	11/2000	Vaartstra	6,488,984 B1	12/2002	Wada et al.
6,150,628 A	11/2000	Smith et al.	6,494,959 B1	12/2002	Samoilov et al.
6,153,935 A	11/2000	Edelstein et al.	6,500,728 B1	12/2002	Wang
6,165,912 A	12/2000	McConnell et al.	6,503,843 B1	1/2003	Xia et al.
6,167,834 B1	1/2001	Wang et al.	6,506,291 B2	1/2003	Tsai et al.
6,169,021 B1	1/2001	Akram et al.	6,516,815 B1	2/2003	Stevens et al.
6,170,428 B1	1/2001	Redeker et al.	6,527,968 B1	3/2003	Wang et al.
6,171,661 B1	1/2001	Zheng et al.	6,528,409 B1	3/2003	Lopatin et al.
6,174,812 B1	1/2001	Hsuing et al.	6,531,377 B2	3/2003	Knorr et al.
6,176,198 B1	1/2001	Kao et al.	6,537,733 B2	3/2003	Campana et al.
6,177,245 B1	1/2001	Ward et al.	6,541,397 B1	4/2003	Bencher
6,179,924 B1	1/2001	Zhao et al.	6,541,671 B1	4/2003	Martinez et al.
6,180,523 B1	1/2001	Lee et al.	6,544,340 B2	4/2003	Yudovsky
6,182,602 B1	2/2001	Redeker et al.	6,547,977 B1	4/2003	Yan et al.
6,189,483 B1	2/2001	Ishikawa et al.	6,551,924 B1	4/2003	Dalton et al.
6,190,233 B1	2/2001	Hong et al.	6,565,729 B2	5/2003	Chen et al.
6,191,026 B1	2/2001	Rana et al.	6,569,773 B1	5/2003	Gellrich et al.
6,194,038 B1	2/2001	Rossmann	6,573,030 B1	6/2003	Fairbairn et al.
6,197,181 B1	3/2001	Chen	6,573,606 B2	6/2003	Sambucetti et al.
6,197,364 B1	3/2001	Paunovic et al.	6,596,602 B2	7/2003	Iizuka et al.
			6,596,654 B1	7/2003	Bayman et al.
			6,602,434 B1	8/2003	Hung et al.
			6,603,269 B1	8/2003	Vo et al.
			6,605,874 B2	8/2003	Leu et al.

(56)

References Cited

U.S. PATENT DOCUMENTS

6,616,967	B1	9/2003	Test	7,709,396	B2	5/2010	Bencher et al.
6,627,532	B1	9/2003	Gaillard et al.	7,722,925	B2	5/2010	White et al.
6,638,810	B2	10/2003	Bakli et al.	7,785,672	B2	8/2010	Choi et al.
6,645,301	B2	11/2003	Sainty et al.	7,807,578	B2	10/2010	Bencher et al.
6,645,550	B1	11/2003	Cheung et al.	7,871,926	B2	1/2011	Xia et al.
6,656,831	B1	12/2003	Lee et al.	7,910,491	B2	3/2011	Soo Kwon et al.
6,656,837	B2	12/2003	Xu et al.	7,915,139	B1	3/2011	Lang et al.
6,677,242	B1	1/2004	Liu et al.	7,939,422	B2	5/2011	Ingle et al.
6,677,247	B2	1/2004	Yuan et al.	7,968,441	B2	6/2011	Xu
6,679,981	B1	1/2004	Pan et al.	7,981,806	B2	7/2011	Jung
6,717,189	B2	4/2004	Inoue et al.	8,008,166	B2	8/2011	Sanchez et al.
6,720,213	B1	4/2004	Gambino et al.	8,058,179	B1	11/2011	Draeger et al.
6,740,585	B2	5/2004	Yoon et al.	8,071,482	B2	12/2011	Kawada
6,743,473	B1	6/2004	Parkhe et al.	8,074,599	B2	12/2011	Choi et al.
6,743,732	B1	6/2004	Lin et al.	8,083,853	B2	12/2011	Choi et al.
6,759,261	B2	7/2004	Shimokohbe et al.	8,187,486	B1	5/2012	Liu et al.
6,762,127	B2	7/2004	Boiteux et al.	8,211,808	B2	7/2012	Sapre et al.
6,762,435	B2	7/2004	Towle	8,309,440	B2	11/2012	Sanchez et al.
6,764,958	B1	7/2004	Nemani et al.	8,328,939	B2	12/2012	Choi et al.
6,765,273	B1	7/2004	Chau et al.	8,435,902	B2	5/2013	Tang et al.
6,772,827	B2	8/2004	Keller et al.	8,951,429	B1 *	2/2015	Liu et al. 216/76
6,794,290	B1	9/2004	Papasouliotis et al.	2001/0015261	A1	8/2001	Kobayashi et al.
6,794,311	B2	9/2004	Huang et al.	2001/0028922	A1	10/2001	Sandhu
6,796,314	B1	9/2004	Graff et al.	2001/0030366	A1	10/2001	Nakano et al.
6,800,830	B2	10/2004	Mahawili	2001/0034121	A1	10/2001	Fu et al.
6,802,944	B2	10/2004	Ahmad et al.	2001/0041444	A1	11/2001	Shields et al.
6,808,564	B2	10/2004	Dietze	2002/0011210	A1	1/2002	Satoh et al.
6,808,748	B2	10/2004	Kapoor et al.	2002/0016080	A1	2/2002	Khan et al.
6,821,571	B2	11/2004	Huang	2002/0016085	A1	2/2002	Huang et al.
6,823,589	B2	11/2004	White et al.	2002/0028585	A1	3/2002	Chung et al.
6,830,624	B2	12/2004	Janakiraman et al.	2002/0029747	A1	3/2002	Powell et al.
6,835,995	B2	12/2004	Li	2002/0033233	A1	3/2002	Savas
6,846,745	B1	1/2005	Papasouliotis et al.	2002/0036143	A1	3/2002	Segawa et al.
6,867,141	B2	3/2005	Jung et al.	2002/0045966	A1	4/2002	Lee et al.
6,869,880	B2	3/2005	Krishnaraj et al.	2002/0054962	A1	5/2002	Huang
6,878,206	B2	4/2005	Tzu et al.	2002/0069820	A1	6/2002	Yudovsky
6,879,981	B2	4/2005	Rothschild et al.	2002/0098681	A1	7/2002	Hu et al.
6,893,967	B1	5/2005	Wright et al.	2002/0177322	A1	11/2002	Li et al.
6,903,031	B2	6/2005	Karim et al.	2002/0187655	A1	12/2002	Tan et al.
6,903,511	B2	6/2005	Chistyakov	2002/0197823	A1	12/2002	Yoo et al.
6,908,862	B2	6/2005	Li et al.	2003/0010645	A1	1/2003	Ting et al.
6,911,112	B2	6/2005	An et al.	2003/0019428	A1	1/2003	Ku et al.
6,911,401	B2	6/2005	Khandan et al.	2003/0029566	A1	2/2003	Roth
6,921,556	B2	7/2005	Shimizu et al.	2003/0029715	A1	2/2003	Yu et al.
6,924,191	B2	8/2005	Liu et al.	2003/0032284	A1	2/2003	Enomoto et al.
6,942,753	B2	9/2005	Choi et al.	2003/0038127	A1	2/2003	Liu et al.
6,951,821	B2	10/2005	Hamelin et al.	2003/0038305	A1	2/2003	Wasshuber
6,958,175	B2	10/2005	Sakamoto et al.	2003/0072639	A1	4/2003	White et al.
6,958,286	B2	10/2005	Chen et al.	2003/0075808	A1	4/2003	Inoue et al.
6,974,780	B2	12/2005	Schuegraf	2003/0077909	A1	4/2003	Jiwari
7,017,269	B2	3/2006	White et al.	2003/0079686	A1	5/2003	Chen et al.
7,030,034	B2	4/2006	Fucsko et al.	2003/0087531	A1	5/2003	Kang et al.
7,049,200	B2	5/2006	Arghavani et al.	2003/0091938	A1	5/2003	Fairbairn et al.
7,078,312	B1	7/2006	Sutanto et al.	2003/0098125	A1	5/2003	An
7,081,414	B2	7/2006	Zhang et al.	2003/0109143	A1	6/2003	Hsieh et al.
7,084,070	B1	8/2006	Lee et al.	2003/0116087	A1	6/2003	Nguyen et al.
7,115,525	B2	10/2006	Abatchev et al.	2003/0116439	A1	6/2003	Seo et al.
7,122,949	B2	10/2006	Strikovski	2003/0121608	A1	7/2003	Chen et al.
7,183,214	B2	2/2007	Nam et al.	2003/0124842	A1	7/2003	Hytros et al.
7,196,342	B2	3/2007	Ershov et al.	2003/0129106	A1	7/2003	Sorensen et al.
7,205,240	B2	4/2007	Karim et al.	2003/0129827	A1	7/2003	Lee et al.
7,223,701	B2	5/2007	Min et al.	2003/0132319	A1	7/2003	Hytros et al.
7,226,805	B2	6/2007	Hallin et al.	2003/0148035	A1	8/2003	Lingampalli
7,253,123	B2	8/2007	Arghavani et al.	2003/0173333	A1	9/2003	Wang et al.
7,256,370	B2	8/2007	Guiver	2003/0173347	A1	9/2003	Guiver
7,288,482	B2	10/2007	Panda et al.	2003/0181040	A1	9/2003	Ivanov et al.
7,341,633	B2	3/2008	Lubomirsky et al.	2003/0183244	A1	10/2003	Rossman
7,390,710	B2	6/2008	Derderian et al.	2003/0190426	A1	10/2003	Padhi et al.
7,396,480	B2	7/2008	Kao et al.	2003/0199170	A1	10/2003	Li
7,465,358	B2	12/2008	Weidman et al.	2003/0221780	A1	12/2003	Lei et al.
7,484,473	B2	2/2009	Keller et al.	2003/0224217	A1	12/2003	Byun et al.
7,488,688	B2	2/2009	Chung et al.	2003/0224617	A1	12/2003	Baek et al.
7,494,545	B2	2/2009	Lam et al.	2004/0005726	A1	1/2004	Huang
7,581,511	B2	9/2009	Mardian et al.	2004/0033678	A1	2/2004	Arghavani et al.
7,628,897	B2	12/2009	Mungekar et al.	2004/0069225	A1	4/2004	Fairbairn et al.
				2004/0070346	A1	4/2004	Choi
				2004/0072446	A1	4/2004	Liu et al.
				2004/0101667	A1	5/2004	O'Loughlin et al.
				2004/0110354	A1	6/2004	Natzle et al.

(56)

References Cited

U.S. PATENT DOCUMENTS

2004/0115876	A1	6/2004	Goundar et al.	2008/0124919	A1	5/2008	Huang et al.
2004/0129224	A1	7/2004	Yamazaki	2008/0124937	A1	5/2008	Xu et al.
2004/0137161	A1	7/2004	Segawa et al.	2008/0142483	A1	6/2008	Hua et al.
2004/0154535	A1	8/2004	Chen et al.	2008/0160210	A1	7/2008	Yang et al.
2004/0175929	A1	9/2004	Schmitt et al.	2008/0162781	A1	7/2008	Haller et al.
2004/0182315	A1	9/2004	Laflamme et al.	2008/0182381	A1	7/2008	Kiyotoshi
2004/0192032	A1	9/2004	Ohmori et al.	2008/0182382	A1	7/2008	Ingle et al.
2004/0194799	A1	10/2004	Kim et al.	2008/0233709	A1	9/2008	Conti et al.
2004/0211357	A1	10/2004	Gadgil et al.	2008/0261404	A1	10/2008	Kozuka et al.
2004/0219789	A1	11/2004	Wood et al.	2008/0268645	A1	10/2008	Kao et al.
2004/0245091	A1	12/2004	Karim et al.	2008/0292798	A1	11/2008	Huh et al.
2005/0001276	A1	1/2005	Gao et al.	2009/0045167	A1	2/2009	Maruyama
2005/0003676	A1	1/2005	Ho et al.	2009/0104738	A1	4/2009	Ring et al.
2005/0009358	A1	1/2005	Choi et al.	2009/0104764	A1	4/2009	Xia et al.
2005/0026430	A1	2/2005	Kim et al.	2009/0104782	A1	4/2009	Lu et al.
2005/0026431	A1	2/2005	Kazumi et al.	2009/0255902	A1	10/2009	Satoh et al.
2005/0035455	A1	2/2005	Hu et al.	2009/0275205	A1	11/2009	Kiehlbauch et al.
2005/0048801	A1	3/2005	Karim et al.	2009/0275206	A1	11/2009	Katz et al.
2005/0090120	A1	4/2005	Hasegawa et al.	2010/0059889	A1	3/2010	Gosset et al.
2005/0098111	A1	5/2005	Shimizu et al.	2010/0075503	A1	3/2010	Bencher et al.
2005/0112901	A1	5/2005	Ji et al.	2010/0093151	A1	4/2010	Arghavani et al.
2005/0121750	A1	6/2005	Chan et al.	2010/0098884	A1	4/2010	Balseanu et al.
2005/0164479	A1*	7/2005	Peng et al. 438/591	2010/0099236	A1	4/2010	Kwon et al.
2005/0181588	A1	8/2005	Kim	2010/0099263	A1	4/2010	Kao et al.
2005/0199489	A1	9/2005	Stevens et al.	2010/0105209	A1	4/2010	Winniczek et al.
2005/0205110	A1	9/2005	Kao et al.	2010/0173499	A1	7/2010	Tao et al.
2005/0218507	A1	10/2005	Kao et al.	2010/0187534	A1	7/2010	Nishi et al.
2005/0221552	A1	10/2005	Kao et al.	2011/0008950	A1	1/2011	Xu
2005/0230350	A1	10/2005	Kao et al.	2011/0053380	A1	3/2011	Sapre et al.
2005/0236694	A1	10/2005	Wu et al.	2011/0143542	A1	6/2011	Feurprier et al.
2005/0266622	A1	12/2005	Arghavani et al.	2011/0151674	A1	6/2011	Tang et al.
2005/0266691	A1	12/2005	Gu et al.	2011/0151676	A1	6/2011	Ingle et al.
2005/0287771	A1	12/2005	Seamons et al.	2011/0151677	A1	6/2011	Wang et al.
2006/0000805	A1	1/2006	Todorow et al.	2011/0165771	A1	7/2011	Ring et al.
2006/0019456	A1	1/2006	Bu et al.	2011/0226734	A1	9/2011	Sumiya et al.
2006/0019486	A1	1/2006	Yu et al.	2011/0230052	A1	9/2011	Tang et al.
2006/0024956	A1	2/2006	Zhijian et al.	2011/0266252	A1	11/2011	Thadani et al.
2006/0033678	A1	2/2006	Lubomirsky et al.	2011/0294300	A1	12/2011	Zhang et al.
2006/0046419	A1	3/2006	Sandhu et al.	2012/0009796	A1	1/2012	Cui et al.
2006/0046484	A1	3/2006	Abatchev et al.	2012/0196447	A1	8/2012	Yang et al.
2006/0051966	A1	3/2006	Or et al.	2012/0211462	A1*	8/2012	Zhang et al. 216/13
2006/0051968	A1	3/2006	Joshi et al.	2012/0228642	A1*	9/2012	Aube et al. 257/79
2006/0093756	A1	5/2006	Rajagopalan et al.	2012/0238102	A1	9/2012	Zhang et al.
2006/0102076	A1	5/2006	Smith et al.	2012/0238103	A1*	9/2012	Zhang et al. 438/720
2006/0130971	A1	6/2006	Chang et al.	2012/0285621	A1	11/2012	Tan
2006/0166107	A1	7/2006	Chen et al.	2013/0034968	A1	2/2013	Zhang et al.
2006/0166515	A1	7/2006	Karim et al.	2013/0045605	A1	2/2013	Wang et al.
2006/0185592	A1	8/2006	Matsuura	2013/0052827	A1	2/2013	Wang et al.
2006/0207504	A1	9/2006	Hasebe et al.	2013/0059440	A1	3/2013	Wang et al.
2006/0211260	A1	9/2006	Tran et al.	2013/0089988	A1*	4/2013	Wang et al. 438/719
2006/0216923	A1	9/2006	Tran et al.	2014/0256131	A1*	9/2014	Wang et al. 438/676
2006/0240661	A1	10/2006	Annapragada et al.				
2006/0246217	A1	11/2006	Weidman et al.				
2006/0251800	A1	11/2006	Weidman et al.				
2006/0251801	A1	11/2006	Weidman et al.				
2006/0252252	A1	11/2006	Zhu et al.				
2006/0261490	A1	11/2006	Su et al.				
2006/0264003	A1	11/2006	Eun				
2006/0264043	A1	11/2006	Stewart et al.				
2007/0071888	A1	3/2007	Shanmugasundram et al.				
2007/0072408	A1	3/2007	Enomoto et al.				
2007/0099431	A1	5/2007	Li				
2007/0099438	A1	5/2007	Ye et al.				
2007/0107750	A1	5/2007	Sawin et al.				
2007/0108404	A1	5/2007	Stewart et al.				
2007/0111519	A1	5/2007	Lubomirsky et al.				
2007/0123051	A1	5/2007	Arghavani et al.				
2007/0181057	A1	8/2007	Lam et al.				
2007/0197028	A1	8/2007	Byun et al.				
2007/0232071	A1	10/2007	Balseanu et al.				
2007/0238321	A1	10/2007	Futase et al.				
2007/0269976	A1	11/2007	Futase et al.				
2007/0281106	A1	12/2007	Lubomirsky et al.				
2008/0085604	A1	4/2008	Hoshino et al.				
2008/0099431	A1	5/2008	Kumar et al.				

FOREIGN PATENT DOCUMENTS

CN	101465386	A	6/2009
EP	0329406		8/1989
EP	0376252		7/1990
EP	0475567		3/1992
EP	0 496 543	A2	7/1992
EP	0 658 928	A1	6/1995
EP	0697467		2/1996
EP	0913498		5/1999
EP	1099776		5/2001
EP	1107288		6/2001
EP	1496542		1/2005
EP	1568797		8/2005
GB	2285174		6/1995
JP	61-276977	A	12/1986
JP	2058836	A	2/1990
JP	02-121330		5/1990
JP	02256235		10/1990
JP	4-239750		7/1992
JP	4-341568	A	11/1992
JP	07-130713	A	5/1995
JP	7-161703	A	6/1995
JP	7297543		11/1995
JP	08-306671		11/1996
JP	09153481	A	6/1997
JP	09-205140	A	8/1997

(56)

References Cited

FOREIGN PATENT DOCUMENTS

JP	10-178004	6/1998	
JP	11124682	5/1999	
JP	H11-204442	7/1999	
JP	2000-012514	1/2000	
JP	2001-308023	11/2001	
JP	2002-100578	4/2002	
JP	2002-141349	5/2002	
JP	2002-222861	8/2002	
JP	2002-256235	9/2002	
JP	2003-019433	1/2003	
JP	2003-059914	2/2003	
JP	2003-179038	6/2003	
JP	2003-217898	7/2003	
JP	2003-318158	11/2003	
JP	2003-347278	12/2003	
JP	2004-047956	2/2004	
JP	2004-156143	6/2004	
JP	04-239723 A	8/2004	
JP	2005-033023 A	2/2005	
JP	2007-173383	7/2007	
JP	08-148470 A	6/2008	
JP	2010-154699	8/2010	
KR	10-0155601	12/1998	
KR	10-0236219	12/1999	
KR	10-2000-0008278	2/2000	
KR	2000-0044928	7/2000	
KR	2001-0014064	2/2001	
KR	10-2001-0049274	6/2001	
KR	10-2001-0058774 A	7/2001	
KR	10-2001-0082109	8/2001	
KR	20030054726 A *	7/2003 H01L 21/302
KR	1020030081177	10/2003	
KR	10-2004-0049739	6/2004	
KR	10-2004-0096365 A	11/2004	
KR	10-2005-0042701	5/2005	
KR	10-2008-0063988	7/2008	
KR	10-2010-0013980	2/2010	
KR	10-2010-0074508 A	7/2010	
KR	10-1050454	7/2011	
KR	10-2011-0126675	11/2011	
KR	10-2012-0082640	7/2012	
WO	92/20833 A1	11/1992	
WO	99/26277	5/1999	
WO	99/54920	10/1999	
WO	99/62108 A2	12/1999	
WO	00/13225 A1	3/2000	
WO	00/22671	4/2000	
WO	01/94719	12/2001	
WO	02083981	10/2002	
WO	03014416	2/2003	
WO	1020030096140	12/2003	
WO	2004/006303	1/2004	
WO	2004/074932	9/2004	
WO	2004/114366 A2	12/2004	
WO	2005036615	4/2005	
WO	2006/069085 A2	6/2006	
WO	2009/071627	6/2009	
WO	2011/087580 A1	7/2011	
WO	2011/115761 A2	9/2011	
WO	2011/139435 A2	11/2011	
WO	2012/018449 A2	2/2012	
WO	2012/125654 A2	9/2012	

OTHER PUBLICATIONS

Abraham, "Reactive Facet Tapering of Plasma Oxide for Multilevel Interconnect Applications", IEEE, V-MIC Conference, Jun. 15-16, 1987, pp. 115-121.

Applied Materials, Inc., "Applied Siconi™ Preclean," printed on Aug. 7, 2009, 8 pages.

Carlson, et al., "A Negative Spacer Lithography Process for Sub-100nm Contact Holes and Vias", University of California at Berkeley, Jun. 19, 2007, 4 pp.

Chang et al. "Frequency Effects and Properties of Plasma Deposited Fluorinated Silicon Nitride", J. Vac Sci Technol B 6(2), Mar./Apr. 1988, pp. 524-532.

Cheng, et al., "New Test Structure to Identify Step Coverage Mechanisms in Chemical Vapor Deposition of Silicon Dioxide," Appl. Phys. Lett., 58 (19), May 13, 1991, p. 2147-2149.

C.K. Hu, et al. "Reduced Electromigration of Cu Wires by Surface Coating" Applied Physics Letters, vol. 81, No. 10, Sep. 2, 2002—pp. 1782-1784.

European Search Report dated May 23, 2006 for EP Application No. 05251143.3.

European Examination Report dated Nov. 13, 2007 for EP Application No. 05251143.3.

EP Partial Search Report, Application No. 08150111.601235/1944796, dated Aug. 22, 2008.

Examination Report dated Jun. 28, 2010 for European Patent Application No. 05251143.3.

Eze, F. C., "Electroless deposition of CoO thin films," J. Phys. D: Appl. Phys. 32 (1999), pp. 533-540.

Fukada et al. "Preparation of SiOF Films with Low Dielectric Constant by ECR Plasma CVD", ISMIC, DUMIC Conference, Feb. 21-22, 1995, pp. 43-49.

Galiano et al. "Stress-Temperature Behavior of Oxide Films Used for Intermetal Dielectric Applications", VMIC Conference, Jun. 9-10, 1992, pp. 100-106.

Hashim et al.; Characterization of thin oxide removal by RTA Treatment; ICSE 1998 Proc. Nov. 1998, Rangi, Malaysia, pp. 213-216.

Hausmann, et al., "Rapid Vapor Deposition of Highly Conformal Silica Nanolaminates," Science, Oct. 11, 2002, p. 402-406, vol. 298.

Hayasaka, N. et al. "High Quality Low Dielectric Constant SiO₂ CVD Using High Density Plasma," Proceedings of the Dry Process Symposium, 1993, pp. 163-168.

Hwang et al., "Smallest Bit-Line Contact of 76nm pitch on NAND Flash Cell by using Reversal PR (Photo Resist) and SADP (Self-Align Double Patterning) Process," IEEE/SEMI Advanced Semiconductor Manufacturing Conference, 2007, 3 pages.

Iijima, et al., "Highly Selective SiO₂ Etch Employing Inductively Coupled Hydro-Fluorocarbon Plasma Chemistry for Self Aligned Contact Etch", Jpn. J. Appl. Phys., Sep. 1997, pp. 5498-5501, vol. 36, Part 1, No. 9A.

International Search Report and Written Opinion of the International Searching Authority mailed Jul. 3, 2008 (PCT/US05/46226).

International Search Report and Written Opinion for PCT Application No. PCT/US2011/027221, mailed on Nov. 1, 2011, 8 pages.

International Search Report and Written Opinion of PCT/US2010/057676 mailed on Jun. 27, 2011, 9 pages.

International Search Report and Written Opinion of PCT/US2011/030582 mailed Dec. 7, 2011, 9 pages.

International Search Report and Written Opinion of PCT/US2011/064724 mailed on Oct. 12, 2012, 8 pages.

International Search Report and Written Opinion of PCT/US2012/028952 mailed on Oct. 29, 2012, 9 pages.

International Search Report and Written Opinion of PCT/US2012/048842 mailed on Nov. 28, 2012, 10 pages.

International Search Report and Written Opinion of PCT/US2012/053329 mailed on Feb. 15, 2013, 8 pages.

International Search Report and Written Opinion of PCT/US2012/057294 mailed on Mar. 18, 2013, 12 pages.

International Search Report and Written Opinion of PCT/US2012/057358 mailed on Mar. 25, 2013, 10 pages.

International Search Report and Written Opinion of PCT/US2012/058818 mailed on Apr. 1, 2013, 9 pages.

International Search Report and Written Opinion of the International Searching Authority for PCT Application No. PCT/US2012/028957, mailed on Oct. 18, 2012, 9 pages.

International Search Report of PCT/US2009/059743 mailed on Apr. 26, 2010, 4 pages.

International Search report and Written Opinion of PCT/CN2010/000932 dated Mar. 31, 2011.

International Search report and Written Opinion of PCT/CN2012/061726 mailed on May 16, 2013, 3 pages.

International Search Report of PCT/2013/037202 mailed on Aug. 23, 2013, 11 pages.

(56)

References Cited**OTHER PUBLICATIONS**

Japanese Patent Office, Official Action for Application No. 2007-317207 mailed on Dec. 21, 2011, 2 pages.

Jung, et al., "Patterning with amorphous carbon spacer for expanding the resolution limit of current lithography tool", Proc. SPIE, 2007, 9 pages, vol. 6520, 65201C.

Laxman, "Low ϵ Dielectrics: CVD Fluorinated Silicon Dioxides", Semiconductor International, May 1995, pp. 71-74.

Lee, et al., "Dielectric Planarization Techniques for Narrow Pitch Multilevel Interconnects," IEEE, V-MIC Conference Jun. 15-16, 1987, pp. 85-92 (1987).

Lin, et al., "Manufacturing of Cu Electroless Nickel/Sn—Pb Flip Chip Solder Bumps", IEEE Transactions on Advanced Packaging, vol. 22, No. 4 (Nov. 1999), pp. 575-579.

Lopatin, et al., "Thin Electroless barrier for copper films", Part of the SPIE Conference of Multilevel Interconnect technology II, SPIE vol. 3508 (1998), pp. 65-77.

Matsuda, et al., "Dual Frequency Plasma CVD Fluorosilicate Glass Deposition for 0.25 μ m Interlevel Dielectrics", ISMIC, DUMIC Conference Feb. 21-22, 1995, pp. 22-28.

Meeks, Ellen et al., "Modeling of SiO₂ deposition in high density plasma reactors and comparisons of model predictions with experimental measurements," J. Vac. Sci. Technol. A, Mar./Apr. 1998, pp. 544-563, vol. 16(2).

Mukai, et al., "A Study of CD Budget in Spacer Patterning Process", Toshiba, SPIE 2008, Feb. 26, 2008, 12 pages.

Musaka, "Single Step Gap Filling Technology for Subhalf Micron Metal Spacings on Plasma Enhanced TEOS/O₂ Chemical Vapor Deposition System," Extended Abstracts of the 1993 International Conference on Solid State Devices and Materials pages, 1993, 510-512.

Nishino, et al.; Damage-Free Selective Etching of Si Native Oxides Using NH₃/NF₃ and SF₆/H₂O Down-Flow Etching, the Japanese Society of Applied Physics, vol. 74, No. 2, pp. 1345-1348, XP-002491959, Jul. 15, 1993.

Ogawa, et al., "Dry Cleaning Technology for Removal of Silicon Native Oxide Employing Hot NH₃/NF₃ Exposure", Japanese Journal of Applied Physics, pp. 5349-5358, Aug. 2002, vol. 41 Part 1, No. 8.

Ota, et al., "Stress Controlled Shallow Trench Isolation Technology to Suppress the Novel Anti-Isotropic Impurity Diffusion for 45nm-Node High Performance CMOSFETs," Symposium on VLSI Technology Digest of Technical Papers, 2005, pp. 138-139.

Pearlstein, Fred. "Electroless Plating," J. Res. Natl. Bur. Stan., Ch. 31 (1974), pp. 710-747.

Qian, et al., "High Density Plasma Deposition and Deep Submicron Gap Fill with Low Dielectric Constant SiOF Films," ISMIC, DUMIC Conference Feb. 21-22, 1995, pp. 50-56.

Robles, et al., "Effects of RF Frequency and Deposition Rates on the Moisture Resistance of PECVD TEOS-Based Oxide Films", ECS Extended Abstracts, Abstract No. 129, May 1992, pp. 215-216, vol. 92-1.

Saito, et al., "Electroless deposition of Ni—B, Co—B and Ni—Co—B alloys using dimethylamineborane as a reducing agent," Journal of Applied Electrochemistry 28 (1998), pp. 559-563.

Schacham-Diamond, et al., "Electrochemically deposited thin film alloys for ULSI and MEMS applications," Microelectronic Engineering 50 (2000), pp. 525-531.

Schacham-Diamond, et al., "Material properties of electroless 100-200 nm thick CoWP films," Electrochemical Society Proceedings, vol. 99-34, pp. 102-110.

Shapiro, et al., "Dual Frequency Plasma CVD Fluorosilicate Glass: Water Absorption and Stability", ISMIC, DUMIC Conference Feb. 21-22, 1995, pp. 118-123.

Smayling, et al., "APF® Pitch-Halving for 2nm Logic Cells using Gridded Design Rules", proceedings of the SPIE, 2008, 8 pages.

S.M. Sze, VLSI Technology, McGraw-Hill Book Company, pp. 107, 108.

U.S. Appl. No. 60/803,499, filed May 30, 2006, 56 pages.

U.S. Appl. No. 11/875,250, filed Oct. 19, 2007, 36 pages.

Usami, et al., "Low Dielectric Constant Interlayer Using Fluorine-Doped Silicon Oxide", Jpn. J. Appl. Phys., Jan. 19, 1994, pp. 408-412, vol. 33 Part 1, No. 1B.

Vassiliev, et al., "Trends in void-free pre-metal CVD dielectrics," Solid State Technology, Mar. 2001, pp. 129-136.

Wang et al.; Ultra High-selectivity silicon nitride etch process using an inductively coupled plasma source; J. Vac. Sci. Technol. A 16(3), May/Jun. 1998, pp. 1582-1587.

Weston, et al., "Ammonium Compounds," Kirk-Othmer Encyclopedia of Chemical Technology, 2003, 30 pages see pp. 717-718, John Wiley & Sons, Inc.

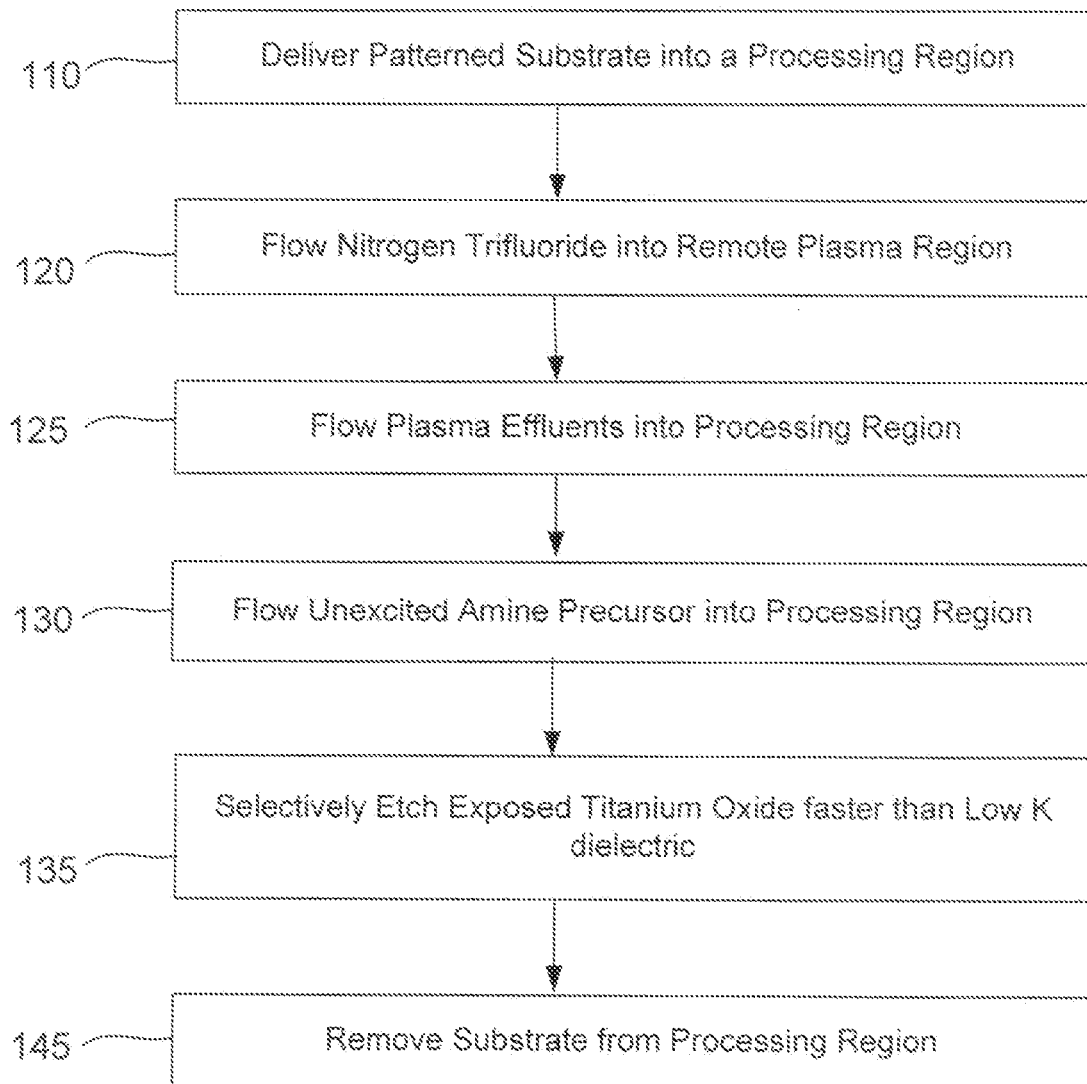
Wolf et al.; Silicon Processing for the VLSI Era; vol. 1; 1986; Lattice Press, pp. 546, 547, 618, 619.

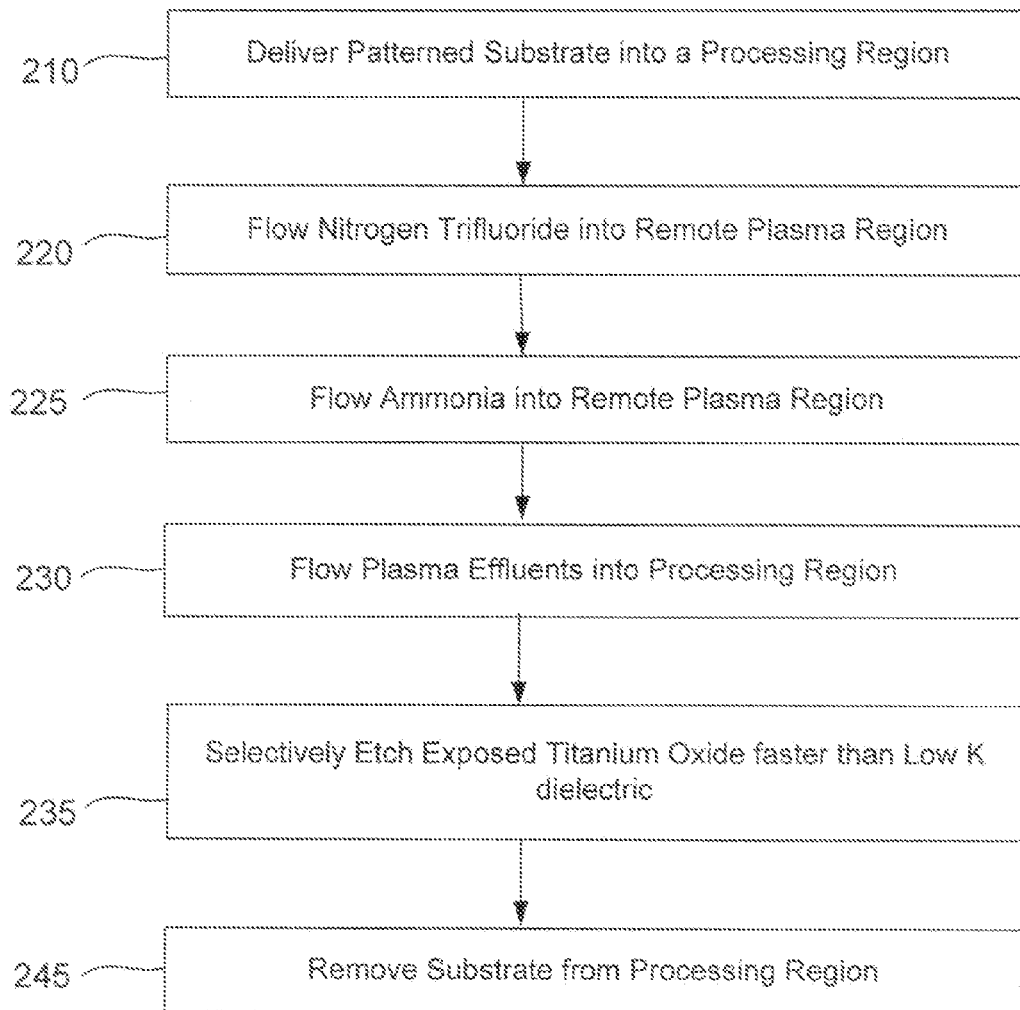
Yosi Shacham-Diamond, et al., "High Aspect Ratio Quarter-Micron Electroless Copper Integrated Technology", Microelectronic Engineering 37/38 (1997) pp. 77-88.

Yu, et al., "Step Coverage Study of PECVD Deposition for Intermetal Dielectric Applications," abstract, VMIC conference, Jun. 12-13, 1990, 7 pages, No. 82.

Yutaka, et al., "Selective Etching of Silicon Native Oxide with Remote-Plasma-Excited Anhydrous Hydrogen Fluoride," Japanese Journal of Applied Physics, 1998, vol. 37, pp. L536-L538.

* cited by examiner

**FIG. 1**

**FIG. 2**

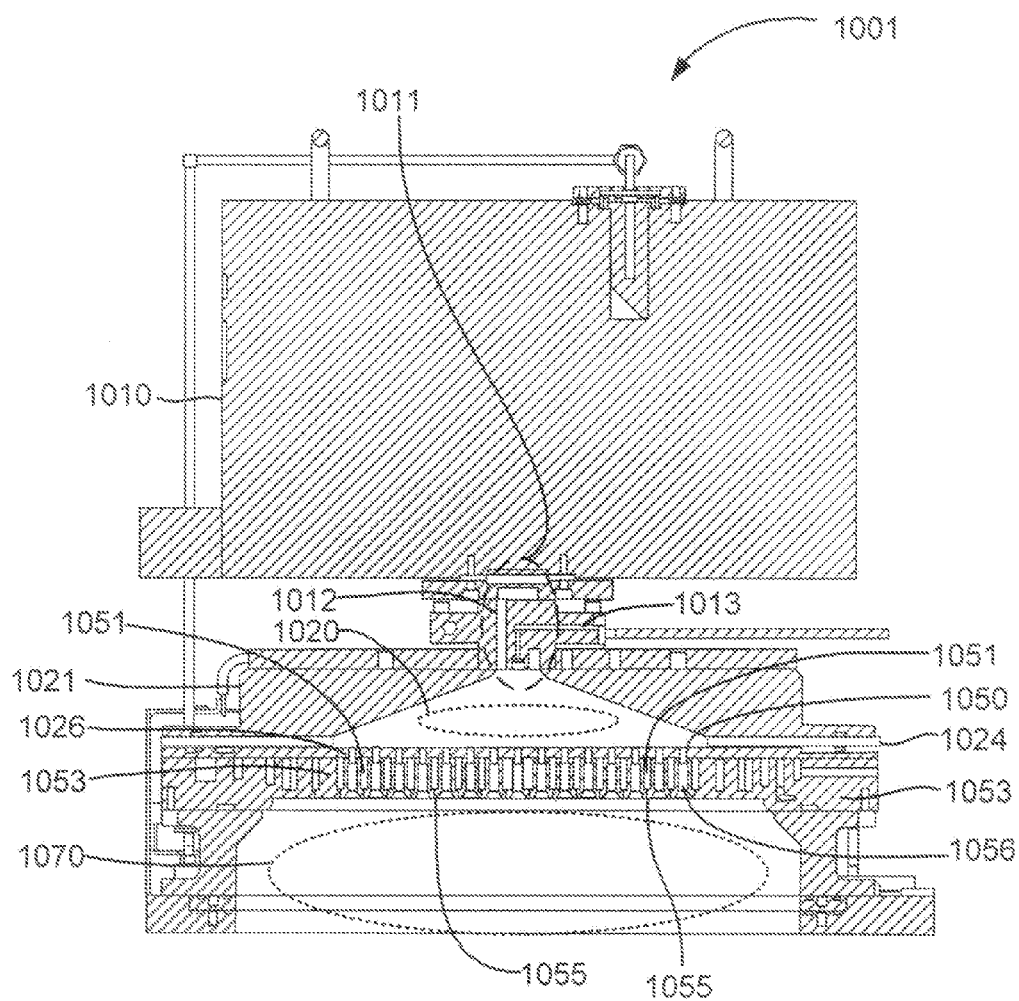


FIG. 3A

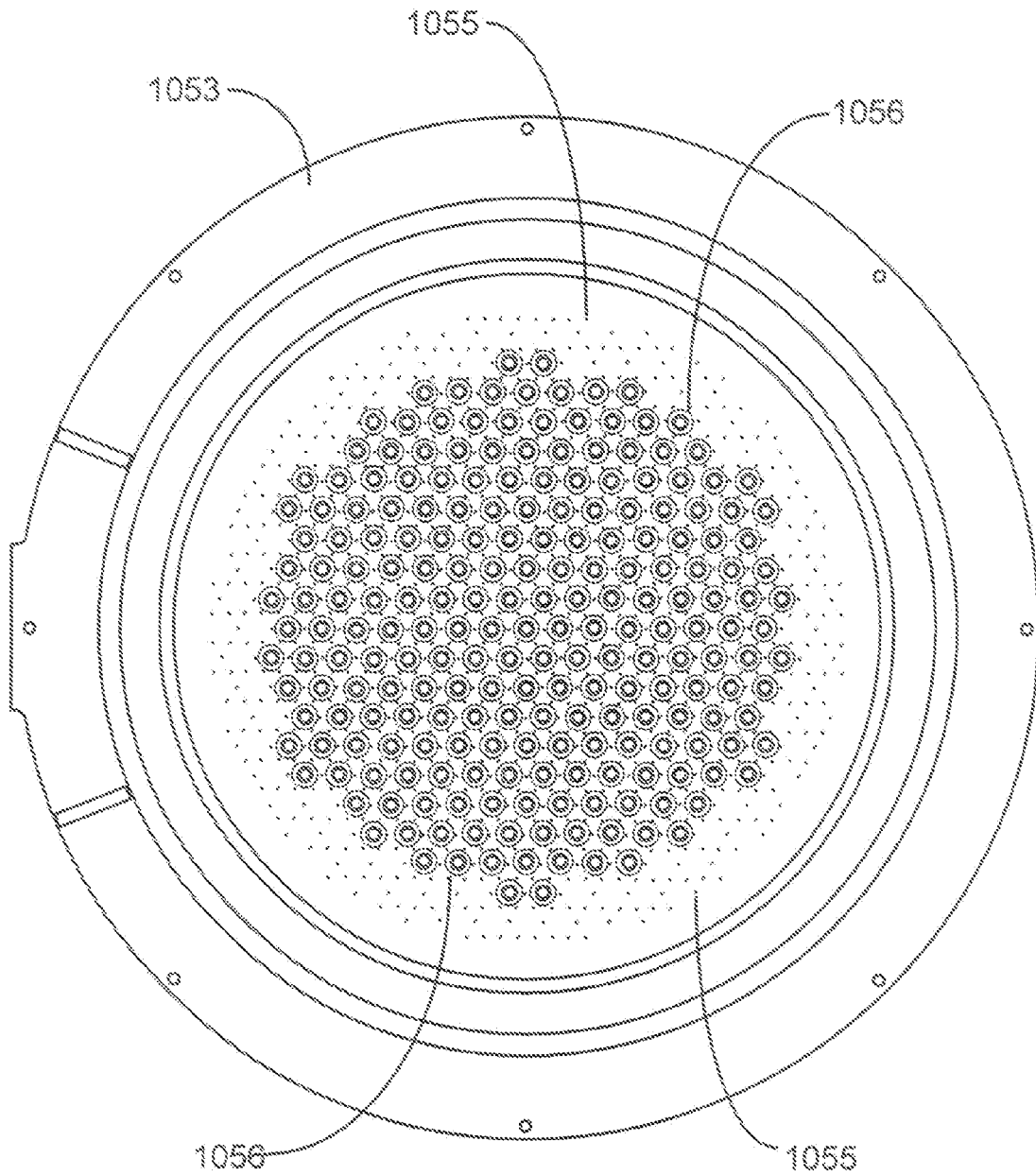


FIG. 3B

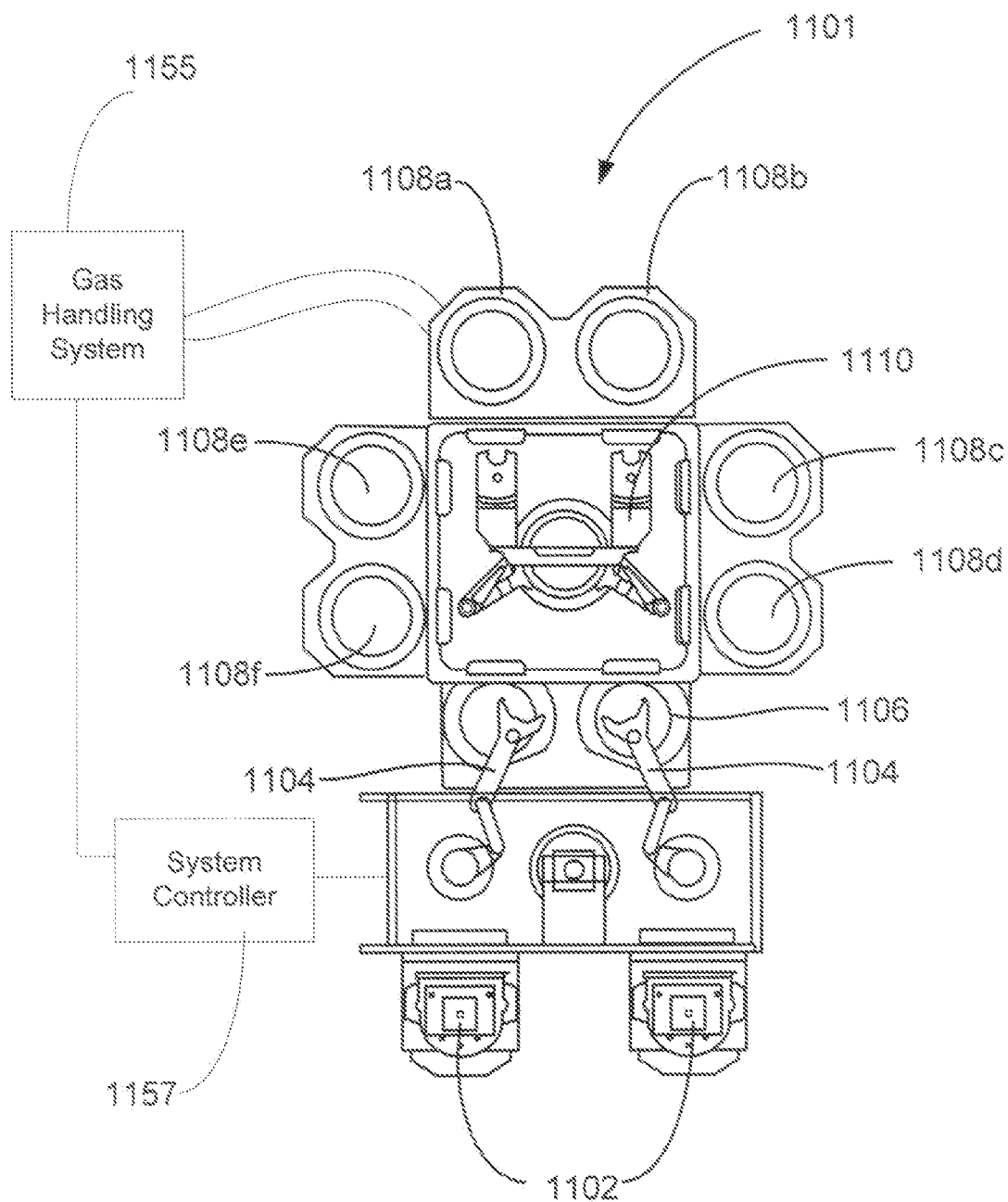


FIG. 4

1

NON-LOCAL PLASMA OXIDE ETCH**CROSS-REFERENCES TO RELATED APPLICATIONS**

This application claims the benefit of U.S. Prov. Pat. App. No. 61/738,855 filed Dec. 18, 2012, and titled "NON-LOCAL PLASMA OXIDE ETCH," which is incorporated in its entirety herein by reference for all purposes.

BACKGROUND OF THE INVENTION

Integrated circuits are made possible by processes which produce intricately patterned material layers on substrate surfaces. Producing patterned material on a substrate requires controlled methods for removal of exposed material. Chemical etching is used for a variety of purposes including transferring a pattern in photoresist into underlying layers, thinning layers or thinning lateral dimensions of features already present on the surface. Often it is desirable to have an etch process which etches one material faster than another helping e.g. a pattern transfer process proceed. Such an etch process is said to be selective to the first material. As a result of the diversity of materials, circuits and processes, etch processes have been developed with a selectivity towards a variety of materials. However, there are few options for selectively etching silicon nitride rather than silicon.

Dry etch processes are often desirable for selectively removing material from semiconductor substrates. The desirability stems from the ability to gently remove material from miniature structures with minimal physical disturbance. Dry etch processes also allow the etch rate to be abruptly stopped by removing the gas phase reagents. Some dry-etch processes involve the exposure of a substrate to remote plasma by-products formed from one or more precursors. For example, remote plasma excitation of ammonia and nitrogen trifluoride enables silicon oxide to be selectively removed from a patterned substrate when the plasma effluents are flowed into the substrate processing region. Remote plasma etch processes have recently been developed to selectively remove a variety of dielectrics relative to one another. However, fewer dry-etch processes have been developed to selectively remove metals and/or their oxidation.

Methods are needed to selectively etch oxide layers from metal surfaces using dry etch processes.

BRIEF SUMMARY OF THE INVENTION

A method of etching exposed titanium oxide, on heterogeneous structures is described and includes a remote plasma etch formed from a fluorine-containing precursor. Plasma effluents from the remote plasma are flowed into a substrate processing region where the plasma effluents may combine with a nitrogen-containing precursor such as an amine (N:) containing precursor. Reactants thereby produced etch the patterned heterogeneous structures with high titanium oxide selectivity while the substrate is at elevated temperature. Titanium oxide etch may alternatively involve supplying a fluorine-containing precursor and a source of nitrogen-and-hydrogen-containing precursor to the remote plasma. The methods may be used to remove titanium oxide while removing little or no low-K dielectric, polysilicon, silicon nitride or titanium nitride.

Embodiments of the invention include methods of etching a substrate in a substrate processing region of a substrate processing chamber. The substrate has an exposed titanium oxide region. The methods include flowing a fluorine-con-

2

taining precursor into a remote plasma region fluidly coupled to the substrate processing region while forming a remote plasma in the remote plasma region to produce plasma effluents. The methods further include flowing a nitrogen-and-hydrogen-containing precursor into the substrate processing region without first passing the nitrogen-and-hydrogen-containing precursor through the remote plasma region. The methods further include etching the exposed titanium oxide region with the combination of the plasma effluents and the nitrogen-and-hydrogen-containing precursor in the substrate processing region.

Embodiments of the invention include methods of etching a substrate in a substrate processing region of a substrate processing chamber. The substrate has an exposed titanium oxide region. The methods include flowing ammonia and a fluorine-containing precursor into a remote plasma region fluidly coupled to the substrate processing region while forming a remote plasma in the remote plasma region to produce plasma effluents. The methods further include etching the exposed titanium oxide region with the plasma effluents in the substrate processing region.

Additional embodiments and features are set forth in part in the description that follows, and in part will become apparent to those skilled in the art upon examination of the specification or may be learned by the practice of the disclosed embodiments. The features and advantages of the disclosed embodiments may be realized and attained by means of the instrumentalities, combinations, and methods described in the specification.

BRIEF DESCRIPTION OF THE DRAWINGS

A further understanding of the nature and advantages of the disclosed embodiments may be realized by reference to the remaining portions of the specification and the drawings.

FIG. 1 is a flow chart of a titanium oxide selective etch process according to disclosed embodiments.

FIG. 2 is a flow chart of a titanium oxide selective etch process according to disclosed embodiments.

FIG. 3A shows a substrate processing chamber according to embodiments of the invention.

FIG. 3B shows a showerhead of a substrate processing chamber according to embodiments of the invention.

FIG. 4 shows a substrate processing system according to embodiments of the invention.

In the appended figures, similar components and/or features may have the same reference label. Further, various components of the same type may be distinguished by following the reference label by a dash and a second label that distinguishes among the similar components. If only the first reference label is used in the specification, the description is applicable to any one of the similar components having the same first reference label irrespective of the second reference label.

DETAILED DESCRIPTION OF THE INVENTION

A method of etching exposed titanium oxide on heterogeneous structures is described and includes a remote plasma etch formed from a fluorine-containing precursor. Plasma effluents from the remote plasma are flowed into a substrate processing region where the plasma effluents may combine with a nitrogen-containing precursor such as an amine (N:) containing precursor. Reactants thereby produced etch the patterned heterogeneous structures with high titanium oxide selectivity while the substrate is at elevated temperature. Titanium oxide etch may alternatively involve supplying a fluo-

3

rine-containing precursor and a source of nitrogen-and-hydrogen-containing precursor to the remote plasma. The methods may be used to remove titanium oxide while removing little or no low-K dielectric, polysilicon, silicon nitride or titanium nitride.

In order to better understand and appreciate the invention, reference is now made to FIG. 1 which is a flow chart of a titanium oxide selective etch process according to disclosed embodiments. Prior to the first operation, the substrate is patterned leaving exposed regions of titanium oxide and regions of low-K dielectric which may be covered. The patterned substrate is then delivered into a substrate processing region (operation 110). A flow of nitrogen trifluoride is initiated into a plasma region separate from the processing region (operation 120). Other sources of fluorine may be used to augment or replace the nitrogen trifluoride. In general, a fluorine-containing precursor is flowed into the plasma region and the fluorine-containing precursor comprises at least one precursor selected from the group consisting of atomic fluorine, diatomic fluorine, nitrogen trifluoride, carbon tetrachloride, hydrogen fluoride and xenon difluoride. The separate plasma region may be referred to as a remote plasma region herein and may be within a distinct module from the processing chamber or a compartment within the processing chamber. The plasma effluents formed in the remote plasma region are then flowed into the substrate processing region (operation 125). At this point, the gas phase etch would have little selectivity towards titanium oxide and would have limited utility. However, a nitrogen-and-hydrogen-containing precursor is simultaneously flowed into the substrate processing region (operation 130) to react with the plasma effluents. The nitrogen-and-hydrogen-containing precursor is not passed through the remote plasma region (or any plasma formed outside the substrate processing region for that matter) and therefore is only excited by interaction with the plasma effluents.

The flow rate of the nitrogen-and-hydrogen-containing precursor may be between 0.5 and about 10 times the flow rate of the fluorine-containing precursor in disclosed embodiments. The flow rate ratio (nitrogen-and-hydrogen-containing precursor:fluorine-containing precursor) may preferably be between 1:1 and 5:1 or between 2:1 and 3:1 in embodiments of the invention. Nitrogen trifluoride (or fluorine-containing precursors in general) may be flowed into the remote plasma region at rates greater than or about 25 sccm, greater than or about 40 sccm, greater than or about 60 sccm or greater than or about 75 sccm in disclosed embodiments.

The patterned substrate is selectively etched (operation 135) such that the titanium oxide is removed at a significantly higher rate than the low-K dielectric. The reactive chemical species are removed from the substrate processing region and then the substrate is removed from the processing region (operation 145). Using the gas phase dry etch processes described herein, the inventors have established that etch selectivities of over 40:1 (titanium oxide etch rate: low-K dielectric etch rate) are possible. The titanium oxide etch rate exceeds the low-K dielectric etch rate by a multiplicative factor of about 50 or more, about 100 or more, about 150 or more, about 200 or more, or about 300 or more, in embodiments of the invention. Low-K dielectric materials may have a dielectric constant less than 3.5, less than 3.3, less than 3.1, or less than 3.0 in disclosed embodiments. Low-K dielectric materials may comprise or consist of silicon, carbon, oxygen and hydrogen.

The gas phase dry etches described herein have also been discovered to increase etch selectivity of titanium oxide relative to silicon (including polysilicon). Using the gas phase dry

4

etch processes described herein, the inventors have established that etch selectivities of over 50:1 (SiO etch rate: Si etch rate) are possible. The titanium oxide etch rate exceeds the (poly)silicon etch rate by a multiplicative factor of about 50 or more, 100 or more, about 150 or more, about 200 or more, or about 300 or more, in embodiments of the invention.

The gas phase dry etches described herein have also been discovered to increase etch selectivity of titanium, oxide relative to silicon nitride (or titanium nitride). Using the gas phase dry etch processes described herein, the inventors have established that etch selectivities of over 50:1 TiO:SiN (or TiO:TiN) are possible. The titanium oxide etch rate exceeds the silicon nitride (or titanium nitride) etch rate by a multiplicative factor of about 50 or more, 100 or more, about 150 or more, about 200 or more, or about 300 or more, in embodiments of the invention.

The nitrogen-and-hydrogen-containing precursor may consist of nitrogen and hydrogen. The nitrogen-and-hydrogen-containing precursor may comprise an amine group, in embodiments of the invention, and may be referred to as an amine-containing precursor. An amine group is defined as having a nitrogen possessing a lone pair of electrons (denoted canonically N:). Therefore nitrogen-and-hydrogen-containing precursors include ammonia, methyl amine, ethylamine, diethylamine, methyl ethyl diamine and the like. Hydrogen-containing precursors may be simultaneously combined with the fluorine-containing precursor in the remote plasma region or prior to entry into the remote plasma region.

Reference is now made to FIG. 2 which is a flow chart of a titanium oxide selective etch process according to alternative disclosed embodiments. Prior to the first operation, the substrate is again patterned leaving exposed regions of titanium oxide and regions of low-K dielectric which may or may not be exposed. The patterned substrate is then delivered into a substrate processing region (operation 210). A flow of nitrogen trifluoride is again initiated into a plasma region separate from the processing region (operation 220). The alternative sources of fluorine may again be used to augment or replace the nitrogen trifluoride. The separate plasma region may be referred to as a remote plasma region, as before, and may be within a distinct module from the processing chamber or a compartment within the processing chamber. Ammonia is also bowed into the remote plasma region (operation 225). This process is similar to the Siconi process with the exception of the exposed substrate materials and some deviations of process parameters as outlined herein. The plasma effluents formed in the remote plasma region are then flowed into the substrate processing region (operation 230).

The patterned substrate is selectively etched (operation 235) such that the titanium oxide is removed at a significantly higher rate than the low-K dielectric. The reactive chemical species are removed from the substrate processing region and then the substrate is removed from the processing region (operation 245). The selectivity embodiments and materials outlined with reference to FIG. 1 also apply to the process of FIG. 2. Substrate temperatures and process pressures also have been found to lie within the same embodiments which will be described shortly. On the other hand, the flow rate ratios may differ as follows. The flow rate of the ammonia may be between 1 and about 20 times the flow rate of the fluorine-containing precursor in disclosed embodiments. The flow rate ratio (ammonia:fluorine-containing precursor) may preferably be between 1:1 and 10:1 or between 3:1 and 7:1 in embodiments of the invention. The absolute flow rate of the fluorine-containing precursor lie within the embodiments of the earlier example.

Without wishing to bind the coverage of the claims to theoretical mechanisms which may or may not be entirely correct, some discussion of possible mechanisms may prove beneficial. Radical-fluorine precursors are produced by delivering a fluorine-containing precursor into the remote plasma region. Applicants suppose that a concentration of fluorine ions and atoms is produced and delivered into the substrate processing region. Ammonia (NH_3) in the plasma or unexcited amine-containing precursors may react with the fluorine to produce less reactive species such as ammonium bifluoride (NH_4HF_2) which travel into the substrate processing region. The delivery of hydrogen and fluorine as described herein allows the formation of solid byproducts (salts) of $(\text{NH}_4)_2\text{TiF}_6$ at relatively low substrate temperatures ($<70^\circ\text{C}$). At higher substrate temperatures, the inventors suppose that the solid by-products are still formed on the exposed titanium oxide (TiO) surfaces but are concurrently removed during the etch process by maintaining the relatively high substrate temperature as outlined herein. By limiting the reactivity of the incoming chemical species, the inventors have found a way to remove titanium oxide while retaining silicon, titanium nitride, low-K dielectric material and silicon nitride on the patterned substrate surface. The selectivity combined with the lack of solid byproducts, make these etch processes well suited for removing titanium oxide structures from above delicate low-K dielectric materials while inducing little deformation in the remaining delicate structures.

During the etch processes described herein, the temperature of the substrate may be about 110°C . or more and about 400°C . or less, in disclosed embodiments. The temperature of the substrate may be above or about 70°C ., above or about 90°C . above or about 110°C ., above or about 130°C ., above or about 150°C . or above or about 170°C . in disclosed embodiments. The temperature of the substrate may be below or about 400°C ., below or about 350°C ., below or about 325°C . or below or about 300°C . in disclosed embodiments. Any of the upper limits can be combined with any of these lower limits to form additional embodiments of the invention. In a preferred embodiment, the temperature of the substrate may be between 200°C . and 300°C . during the etching operation in embodiments of the invention.

The inventors have found that exposed interior components should be kept at elevated temperatures in order to avoid trapping the desirable etching agents (hypothesized to include ammonium bifluoride). Interior components include surfaces which come in contact with the etching agents which are formed in either configuration (see FIGS. 1-2 and associated discussion). Possible interior components will be discussed in greater detail in the exemplary equipment section, but may include a showerhead separating the substrate processing region from the remote plasma region. Interior components may include chamber walls, faceplates and dedicated ion suppression elements. Interior components may be kept above or about 70°C ., above or about 90°C ., above or about 110°C . or above or about 130°C . in disclosed embodiments during the etching operation. Maintaining an elevated temperature of between, for example, 130°C . and 170°C ., has been determined to increase the etch rate of the substrate by ensuring adequate flow of neutral active etching species to the titanium oxide substrate surface.

A dedicated ion suppression element may be included in the remote plasma region in order to further control the ion density entering the substrate processing region. Reducing the ion concentration is believed to enable the high titanium oxide selectivities outlined earlier. The ion suppression element functions to reduce or eliminate ionically charged species traveling from the plasma generation region to the sub-

strate. Uncharged neutral and radical species may pass through the openings in the ion suppressor to react at the substrate.

The pressure in the substrate processing region may be above or about 0.1 Torr and less than or about 50 Torr, in disclosed embodiments, during the etching operation. The pressure may be above or about 0.1 Torr, above or about 0.2 Torr, above or about 0.5 Torr or above or about 1 Torr in disclosed embodiments. The pressure may be below or about 50 Torr, below or about 25 Torr, below or about 15 Torr or below or about 10 Torr in disclosed embodiments. Any of the upper limits can be combined with any of these lower limits to form additional embodiments of the invention. Additional titanium oxide selective etch process parameters are disclosed in the course of describing an exemplary processing chamber and system.

Exemplary Processing System

Processing chambers that may implement embodiments of the present invention may be included within processing platforms such as the CENTURA® and PRODUCER® systems, available from Applied Materials, Inc. of Santa Clara, Calif. Examples of substrate processing chambers that can be used with exemplary methods of the invention may include those shown and described in co-assigned U.S. Provisional Patent App. No. 60/803,499 to Lubomirsky et al, filed May 30, 2006, and titled "PROCESS CHAMBER FOR DIELECTRIC GAFILL," the entire contents of which is herein incorporated by reference for all purposes. Additional exemplary systems may include those shown and described in U.S. Pat. Nos. 6,387,207 and 6,830,624, which are also incorporated herein by reference for all purposes.

FIG. 3A is a substrate processing chamber 1001 according to disclosed embodiments. A remote plasma system (RPS 1010) may process the fluorine-containing precursor which then travels through a gas inlet assembly 1011. Two distinct gas supply channels are visible within the gas inlet assembly 1011. A first channel 1012 carries a gas that passes through the remote plasma system RPS 1010, while a second channel 1013 bypasses the RPS 1010. Either channel may be used for the fluorine-containing precursor, in embodiments. On the other hand, the first channel 1002 may be used for the process gas and the second channel 1013 may be used for a treatment gas. The lid 1021 (e.g. a conducting top portion) and a perforated partition (showerhead 1053) are shown with an insulating ring 1024 in between, which allows an AC potential to be applied to the lid 1021 relative to showerhead 1053. The AC potential strikes a plasma in chamber plasma region 1020. The process gas may travel through first channel 1012 into chamber plasma region 1020 and may be excited by a plasma in chamber plasma region 1020 alone or in combination with RPS 1010. If the process gas (the fluorine-containing precursor) flows through second channel 1013, then only the chamber plasma region 1020 is used for excitation. The combination of chamber plasma region 1020 and/or RPS 1010 may be referred to as a remote plasma system herein. The perforated partition (also referred to as a showerhead) 1053 separates chamber plasma region 1020 from a substrate processing region 1070 beneath showerhead 1053. Showerhead 1053 allows a plasma present in chamber plasma region 1020 to avoid directly exciting gases in substrate processing region 1070, while still allowing excited species to travel from chamber plasma region 1020 into substrate processing region 1070.

Showerhead 1053 is positioned between chamber plasma region 1020 and substrate processing region 1070 and allows plasma effluents (excited derivatives of precursors or other gases) created within RPS 1010 and/or chamber plasma

region 1020 to pass through a plurality of through holes 1056 that traverse the thickness of the plate. The showerhead 1053 also has one or more hollow volumes 1051 which can be filled with a precursor in the form of a vapor or gas (such as an amine-containing precursor) and pass through small holes 1055 into substrate processing region 1070 but not directly into chamber plasma region 1020. Showerhead 1053 is thicker than the length of the smallest diameter 1050 of the through-holes 1056 in this disclosed embodiment in order to maintain a significant concentration of excited species penetrating from chamber plasma region 1020 to substrate processing region 1070, the length 1026 of the smallest diameter 1050 of the through-holes may be restricted by forming larger diameter portions of through-holes 1056 part way through the showerhead 1053. The length of the smallest diameter 1050 of the through-holes 1056 may be the same order of magnitude as the smallest diameter of the through-holes 1056 or less in disclosed embodiments. In this way a fluorine-containing precursor may be flowed through through-holes 1056 in a dual-zone showerhead and a nitrogen-and-hydrogen-containing precursor may pass through separate zones (hollow volumes 1051) in the dual-zone showerhead, wherein the separate zones open into the substrate processing region but not into the remote plasma region.

Showerhead 1053 may be configured to serve the purpose of an ion suppressor as shown in FIG. 3A. Alternatively, a separate processing chamber element may be included (not shown) which suppresses the ion concentration traveling into substrate processing region 1070. Lid 1021 and showerhead 1053 may function as a first electrode and second electrode, respectively, so that lid 1021 and showerhead 1053 may receive different electric voltages. In these configurations, electrical power (e.g., RF power) may be applied to lid 1021, showerhead 1053, or both. For example, electrical power may be applied to lid 1021 while showerhead 1053 (serving as ion suppressor) is grounded. The substrate processing system may include a RF generator that provides electrical power to the lid and/or showerhead 1053. The voltage applied to lid 1021 may facilitate a uniform distribution of plasma (i.e., reduce localized plasma) within chamber plasma region 1020. To enable the formation of a plasma in chamber plasma region 1020, insulating ring 1024 may electrically insulate lid 1021 from showerhead 1053. Insulating ring 1024 may be made from a ceramic and may have a high breakdown voltage to avoid sparking. Portions of substrate processing chamber 1001 near the capacitively-coupled plasma components just described may further include a cooling unit (not shown) that includes one or more cooling fluid channels to cool surfaces exposed to the plasma with a circulating coolant (e.g., water).

In the embodiment shown, showerhead 1053 may distribute (via through-holes 1056) process gases which contain oxygen, hydrogen and/or nitrogen and/or plasma effluents of such process gases upon excitation by a plasma in chamber plasma region 1020. In embodiments, the process gas introduced into the RPS 1010 and/or chamber plasma region 1020 through first channel 1012 may contain fluorine (e.g. CF_4 , NF_3 or XeF_2). The process gas may also include a carrier gas such as helium, argon, nitrogen (N_2), etc. Plasma effluents may include ionized or neutral derivatives of the process gas and may also be referred to herein as a radical-fluorine precursor referring to the atomic constituent of the process gas introduced.

Through-holes 1056 are configured to suppress the migration of ionically-charged species out of the chamber plasma region 1020 while allowing uncharged neutral or radical species to pass through showerhead 1053 into substrate processing region 1070. These uncharged species may include highly

reactive species that are transported with less reactive carrier gas by through-holes 1056. As noted above, the migration of ionic species by through-holes 1056 may be reduced, and in some instances completely suppressed. Controlling the amount of ionic species passing through showerhead 1053 provides increased control over the gas mixture brought into contact with the underlying wafer substrate, which in turn increases control of the deposition and/or etch characteristics of the gas mixture. For example, adjustments in the ion concentration of the gas mixture can significantly alter its etch selectivity (e.g., TiO_2 :low K dielectric etch ratios).

In embodiments, the number of through-holes 1056 may be between about 60 and about 2000. Through-holes 1056 may have a variety of shapes but are most easily made round. The smallest diameter 1050 of through-holes 1056 may be between about 0.5 mm and about 20 mm or between about 1 mm and about 6 mm in disclosed embodiments. There is also latitude in choosing the cross-sectional shape of through-holes, which may be made conical, cylindrical or a combination of the two shapes. The number of small holes 1055 used to introduce a gas into substrate processing region 1070 may be between about 100 and about 5000 or between about 500 and about 2000 in different embodiments. The diameter of the small holes 1055 may be between about 0.1 mm and about 2 mm.

FIG. 3B is a bottom view of a showerhead 1053 for use with a processing chamber according to disclosed embodiments. Showerhead 1053 corresponds with the showerhead shown in FIG. 3A. Through-holes 1056 are depleted with a larger inner-diameter (ID) on the bottom of showerhead 1053 and a smaller ID at the top. Small holes 1055 are distributed substantially evenly over the surface of the showerhead, even amongst the through-holes 1056 which helps to provide more even mixing than other embodiments described herein.

An exemplary patterned substrate may be supported by a pedestal (not shown) within substrate processing region 1070 when fluorine-containing plasma effluents arriving through through-holes 1056 in showerhead 1053 combine with ammonia arriving through the small holes 1055 originating from hollow volumes 1051. Though substrate processing region 1070 may be equipped to support a plasma for other processes such as curing, no plasma is present during the etching of patterned substrate, in embodiments of the invention.

A plasma may be ignited either in chamber plasma region 1020 above showerhead 1053 or substrate processing region 1070 below showerhead 1053. A plasma is present in chamber plasma region 1020 to produce the radical-fluorine precursors from an inflow of the fluorine-containing precursor. An AC voltage typically in the radio frequency (RF) range is applied between the conductive top portion 1021 of the processing chamber and showerhead 1053 to ignite a plasma in chamber plasma region 1020 during deposition. An RF power supply generates a high RF frequency of 13.56 MHz but may also generate other frequencies alone or in combination with the 13.56 MHz frequency.

The top plasma may be left at low or no power when the bottom plasma in the substrate processing region 1070 is turned on to either cure a film or clean the interior surfaces bordering substrate processing region 1070. A plasma in substrate processing region 1070 is ignited by applying an AC voltage between showerhead 1053 and the pedestal or bottom of the chamber. A cleaning gas may be introduced into substrate processing region 1070 while the plasma is present.

The pedestal may have a heat exchange channel through which a heat exchange fluid flows to control the temperature of the substrate. This configuration allows the substrate tem-

perature to be cooled or heated to maintain relatively low temperatures (from room temperature through about 120° C.). The heat exchange fluid may comprise ethylene glycol and water. The wafer support platter of the pedestal (preferably aluminum, ceramic, or a combination thereof) may also be resistively heated in order to achieve relatively high temperatures (Horn about 120° C. through about 1100° C.) using an embedded single-loop embedded heater element configured to make two full turns in the form of parallel concentric circles. An outer portion of the heater element may run adjacent to a perimeter of the support platter, while an inner portion runs on the path of a concentric circle having a smaller radius. The wiring to the heater element passes through the stem of the pedestal.

The substrate processing system is controlled by a system controller. In an exemplary embodiment, the system controller includes a hard disk drive, a floppy disk drive and a processor. The processor contains a single-board computer (SBC), analog and digital input/output boards, interface boards and stepper motor controller boards. Various parts of CVD system conform to the Versa Modular European (VME) standard which defines board, card cage, and connector dimensions and types. The VME standard also defines the bus structure as having a 16-bit data bus and a 24-bit address bus.

The system controller controls all of the activities of the etching chamber. The system controller executes system control software, which is a computer program stored in a computer-readable medium. Preferably, the medium is a hard disk drive, but the medium may also be other kinds of memory. The computer program includes sets of instructions that dictate the timing, mixture of gases, chamber pressure, chamber temperature, RF power levels, susceptor position, and other parameters of a particular process. Other computer programs stored on other memory devices including, for example, a floppy disk or other another appropriate drive, may also be used to instruct the system controller.

A process for depositing a film stack on a substrate or a process for cleaning a chamber can be implemented using a computer program product that is executed by the system controller. The computer program code can be written in any conventional computer readable programming language: for example, 68000 assembly language, C, C++, Pascal, Fortran or others. Suitable program code is entered into a single file, or multiple files, using a conventional text editor, and stored or embodied in a computer usable medium, such as a memory system of the computer. If the entered code text is in a high level language, the code is compiled, and the resultant compiler code is then linked with an object code of precompiled Microsoft Windows® library routines. To execute the linked, compiled object code the system user invokes the object code, causing the computer system to load the code in memory. The CPU then reads and executes the code to perform the tasks identified in the program.

The interface between, a user and the controller is via a flat-panel touch-sensitive monitor. In the preferred embodiment two monitors are used, one mounted in the clean room wall for the operators and the other behind the wall for the service technicians. The two monitors may simultaneously display the same information, in which case only one accepts input at a time. To select a particular screen or function, the operator touches a designated area of the touch-sensitive monitor. The touched area changes its highlighted color, or a new menu or screen is displayed, confirming communication between the operator and the touch-sensitive monitor. Other devices, such as a keyboard, mouse, or other pointing or communication device, may be used instead of or in addition

to the touch-sensitive monitor to allow the user to communicate with the system controller.

The chamber plasma region or a region in an RPS may be referred to as a remote plasma region. In embodiments, the radical precursor (e.g. a radical-fluorine precursor) is created in the remote plasma region and travels into the substrate processing region to combine with an amine-containing precursor. In embodiments, the amine-containing precursor is excited only by the radical-fluorine precursor. Plasma power may essentially be applied only to the remote plasma region, in embodiments, to ensure that the radical-fluorine precursor provides the dominant excitation to the amine-containing precursor (e.g. ammonia).

In embodiments employing a chamber plasma region, the excited plasma effluents are generated in a section of the substrate processing region partitioned from a deposition region. The deposition region, also known herein as the substrate processing region, is where the plasma effluents mix and react with the amine-containing precursor to etch the patterned substrate (e.g., a semiconductor wafer). The excited plasma effluents may also be accompanied by inert gases (in the exemplary case, argon). The amine-containing precursor does not pass through a plasma before entering the substrate plasma region, in embodiments. The substrate processing region may be described herein as "plasma-free" during the etch of the patterned substrate. "Plasma-free" does not necessarily mean the region is devoid of plasma. Ionized species and free electrons created within the plasma region do travel through pores (apertures) in the partition (showerhead) but the amine-containing precursor is not substantially excited by the plasma power applied to the plasma region. The borders of the plasma in the chamber plasma region are hard to define and may encroach upon the substrate processing region through the apertures in the showerhead. In the case of an inductively-coupled plasma, a small amount of ionization may be effected within the substrate processing region directly. Furthermore, a low intensity plasma may be created in the substrate processing region without eliminating desirable features of the forming film. All causes for a plasma having much tower intensity ion density than the chamber plasma region (or a remote plasma region, for that matter) during the creation of the excited plasma effluents do not deviate from the scope of "plasma-free" as used herein.

Nitrogen trifluoride (or another fluorine-containing precursor) may be flowed into chamber plasma region **1020** at rates between about 25 sccm and about 200 sccm between about 50 sccm and about 150 sccm or between about 75 sccm and about 125 sccm in different embodiments. Amine-containing precursor may be flowed into substrate processing region **1070** at rates between about 25 sccm and about 200 sccm, between about 50 sccm and about 150 sccm or between about 75 sccm and about 125 sccm in different embodiments.

Combined flow rates of amine-containing precursor and fluorine-containing precursor into the chamber may account for 0.05% to about 20% by volume of the overall gas mixture; the remainder being carrier gases. The fluorine-containing precursor is flowed into the remote plasma region but the plasma effluents has the same volumetric flow ratio, in embodiments. In the case of the fluorine-containing precursor, a purge or carrier gas may be first initiated into the remote plasma region before those of the fluorine-containing gas to stabilize the pressure within the remote plasma region.

Plasma power can be a variety of frequencies or a combination of multiple frequencies. In the exemplary processing system the plasma is provided by RF power delivered to lid **1021** relative to showerhead **1053**. The RF power may be between about 10 watts and about 2000 watts, between about

11

100 watts and about 2000 watts, between about 200 watts and about 1500 watts or between about 500 watts and about 1000 watts in different embodiments. The RF frequency applied its the exemplary processing system may be low RF frequencies less than about 200 kHz, high RF frequencies between about 10 MHz and about 15 MHz or microwave frequencies greater than or about 1 GHz in different embodiments. The plasma power may be capacitively-coupled (CCP) or inductively-coupled (ICP) into the remote plasma region.

Substrate processing region **1070** can be maintained at a variety of pressures during the flow of amine-containing precursor, any carrier gases and plasma effluents into substrate processing region **1070**. The pressure may be maintained between about 500 mTorr and about 30 Torr, between about 1 Torr and about 20 Torr or between about 5 Torr and about 15 Torr in different embodiments.

In one or more embodiments, the substrate processing chamber **1001** can be integrated into a variety of multi-processing platforms, including the Producer™ GT; Centura™ AP and Endura™ platforms available from Applied Materials, Inc. located in Santa Clara, Calif. Such a processing platform is capable of performing several processing operations without breaking vacuum. Processing chambers that may implement embodiments of the present invention may include dielectric etch chambers or a variety of chemical vapor deposition chambers, among other types of chambers.

Embodiments of the deposition systems may be incorporated into larger fabrication systems for producing integrated circuit chips. FIG. 4 shows one such system **1101** of deposition, baking and curing chambers according to disclosed embodiments. In the figure, a pair of FOUPs (front opening unified pods) **1102** supply substrate substrates (e.g., 300 mm diameter wafers) that are received by robotic arms **1104** and placed into a low pressure holding area **1106** before being placed into one of the substrate processing chambers **1108a-f**. A second robotic arm **1110** may be used to transport the substrate wafers from the holding area **1106** to the substrate processing chambers **1108a-f** and back. Each substrate processing chamber **1108a-f**, can be outfitted to perform a number of substrate processing operations including the dry etch processes described herein in addition to cyclical layer deposition (CCD), atomic layer deposition (ALD), chemical vapor deposition (CVD), physical vapor deposition (PVD), etch, pre-clean, degas, orientation and other substrate processes.

The substrate processing chambers **1108a-f** may include one or more system components for depositing, annealing, curing and/or etching a flowable dielectric film on the substrate wafer. In one configuration, two pairs of the processing chamber (e.g., **1108c-d** and **1108e-f**) may be used to deposit dielectric material on the substrate, and the third pair of processing chambers (e.g., **1108a-b**) may be used to etch the deposited dielectric. In another configuration, all three pairs of chambers (e.g., **1108a-f**) may be configured to etch a dielectric film on the substrate. Any one or more of the processes described may be carried out on chamber(s) separated from the fabrication system shown in different embodiments.

System controller **1157** is used to control motors, valves, flow controllers, power supplies and other functions required to carry out process recipes described herein. A gas handling system **1155** may also be controlled by system controller **1157** to introduce gases to one or all of the substrate processing chambers **1108a-f**. System controller **1157** may rely on feedback from optical sensors to determine and adjust the position of movable mechanical assemblies in gas handling system **1155** and/or in substrate processing chambers **1108a-f**. Mechanical assemblies may include the robot, throttle

12

valves and susceptors which are moved by motors under the control of system controller **1157**.

In an exemplary embodiment, system controller **1157** includes a hard disk drive (memory), USB ports, a floppy disk drive and a processor. System controller **1157** includes analog and digital input/output boards, interface boards and stepper motor controller boards. Various parts of multi-chamber processing system **1101** which contains processing chamber **1001** are controlled by system controller **1157**. The system controller executes system control software in the form of a computer program stored on computer-readable medium such as a hard disk, a floppy disk or a flash memory thumb drive. Other types of memory can also be used. The computer program includes sets of instructions that dictate the timing, mixture of gases, chamber pressure, chamber temperature, RF power levels, susceptor position, and other parameters of a particular process.

As used herein “substrate” may be a support substrate with or without layers formed thereon. The patterned substrate may be an insulator or a semiconductor of a variety of doping concentrations and profiles and may, for example, be a semiconductor substrate of the type used in the manufacture of integrated circuits. Exposed “titanium oxide” of the patterned substrate may be predominantly TiO₂ but may include concentrations of other elemental constituents such as nitrogen, hydrogen, carbon and the like. In some embodiments, titanium oxide films etched using the methods disclosed herein consist essentially of titanium and oxygen. Exposed “silicon oxide” of the patterned substrate is predominantly SiO₂ but may include concentrations of other elemental constituents such as nitrogen, hydrogen, carbon and the like. In some embodiments, silicon oxide films etched using the methods disclosed herein consist essentially of silicon and oxygen. The term “precursor” is used to refer to any process gas which takes part in a reaction to either remove material from or deposit material onto a surface. “Plasma effluents” describe gas exiting from the chamber plasma region and entering the substrate processing region. Plasma effluents are in an “excited state” wherein at least some of the gas molecules are in vibrationally-excited, dissociated and/or ionized states. A “radical precursor” is used to describe plasma effluents (a gas in an excited state which is exiting a plasma) which participate in a reaction to either remove material from or deposit material on a surface. A “radical-fluorine precursor” is a radical precursor which contains fluorine but may contain other elemental constituents. The phrase “inert gas” refers to any gas which does not form chemical bonds when etching or being incorporated into a film. Exemplary inert gases include noble gases but may include other gases so long as no chemical bonds are formed when (typically) trace amounts are trapped in a film.

The terms “gap” and “trench” are used throughout with no implication that the etched geometry has a large horizontal aspect ratio. Viewed from above the surface, trenches may appear circular, oval, polygonal, rectangular, or a variety of other shapes. A trench may be in the shape of a moat around an island of material (e.g. a substantially cylindrical TiN pillar). The term “via” is used to refer to a low aspect ratio trench (as viewed from above) which may or may not be filled with metal to form a vertical electrical connection. As used herein, a conformal etch process refers to a generally uniform removal of material on a surface in the same shape as the surface, i.e., the surface of the etched layer and the pre-etch surface are generally parallel. A person having ordinary skill in the art will recognize that the etched interface likely cannot be 100% conformal and thus the term “generally” allows for acceptable tolerances.

13

Having disclosed several embodiments, it will be recognized by those of skill in the art that various modifications, alternative constructions, and equivalents may be used without departing from the spirit of the disclosed embodiments. Additionally, a number of well known processes and elements have not been described in order to avoid unnecessarily obscuring the present invention. Accordingly, the above description should not be taken as limiting the scope of the invention.

Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limits of that range is also specifically disclosed. Each smaller range between any stated value or intervening value in a stated range and any other stated or intervening value in that stated range is encompassed. The upper and lower limits of these smaller ranges may independently be included or excluded in the range, and each range where either, neither or both limits are included in the smaller ranges is also encompassed within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included.

As used herein and in the appended claims, the singular forms "a", "an", and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a process" includes a plurality of such processes and reference to "the dielectric material" includes reference to one or more dielectric materials and equivalents thereof known to those skilled in the art, and so forth.

Also, the words "comprise," "comprising," "include," "including," and "includes" when used in this specification and in the following claims are intended to specify the presence of stated features, integers, components, or steps, but they do not preclude the presence or addition of one or more other features, integers, components, steps, acts, or groups.

What is claimed is:

1. A method of etching a substrate in a substrate processing region of a substrate processing chamber, wherein the substrate has an exposed titanium oxide region, the method comprising:

flowing a fluorine-containing precursor into a remote plasma region fluidly coupled to the substrate processing region while forming a remote plasma in the remote plasma region to produce plasma effluents;

flowing a nitrogen-and-hydrogen-containing precursor into the substrate processing region without first passing the nitrogen-and-hydrogen-containing precursor through the remote plasma region; and

etching the exposed titanium oxide region with the combination of the plasma diluents and the nitrogen-and-hydrogen-containing precursor in the substrate processing region.

2. The method of claim 1 wherein the patterned substrate further comprises a second exposed region selected from the group consisting of an exposed low-K dielectric region, an exposed silicon region, an exposed titanium nitride region or an exposed silicon nitride region and the selectivity of the etching operation (exposed titanium oxide region: second exposed region) is greater than or about 50:1.

3. The method of claim 1 wherein the nitrogen-and-hydrogen-containing precursor comprises an amine-containing precursor.

4. The method of claim 1 wherein the nitrogen-and-hydrogen-containing precursor comprises ammonia.

14

5. The method of claim 1 wherein the substrate processing region is plasma-free while etching the exposed titanium oxide region.

6. The method of claim 1 wherein the nitrogen-and-hydrogen-containing precursor is not excited by any remote plasma formed outside the substrate processing region.

7. The method of claim 1 wherein the fluorine-containing precursor comprises a precursor selected from the group consisting of atomic fluorine, diatomic fluorine, nitrogen trifluoride, hydrogen fluoride and xenon difluoride.

8. The method of claim 1 wherein the operation of flowing the fluorine-containing precursor into the remote plasma region further comprises flowing a hydrogen-containing precursor into the remote plasma region.

9. The method of claim 1 wherein the fluorine-containing precursor flowed through through-holes in a dual-zone showerhead and the nitrogen-and-hydrogen-containing precursor passes through separate zones in the dual-zone showerhead, wherein the separate zones open into the substrate processing region but not into the remote plasma region.

10. The method of claim 1 wherein a temperature of the patterned substrate is greater than or about 70° C. and less than or about 400° C. during the etching operation.

11. The method of claim 1 wherein a temperature of the patterned substrate is greater than or about 150° C. and less than or about 350° C. during the etching operation.

12. A method of etching a substrate in a substrate processing region of a substrate processing chamber, wherein the substrate has an exposed titanium oxide region, the method comprising:

flowing ammonia and a fluorine-containing precursor into a remote plasma region fluidly coupled to the substrate processing region while forming a remote plasma in the remote plasma region to produce plasma effluents; and etching the exposed titanium oxide region with the plasma effluents in the substrate processing region.

13. The method of claim 12 wherein the patterned substrate further comprises a second exposed region selected from the group consisting of an exposed low-K dielectric region, an exposed silicon region, an exposed titanium nitride region or an exposed silicon nitride region and the selectivity of the etching operation (exposed titanium oxide region: second exposed region) is greater than or about 50:1.

14. The method of claim 12 wherein the substrate processing region is plasma-free while etching the exposed titanium oxide region.

15. The method of claim 12 wherein the nitrogen-and-hydrogen-containing precursor is not excited by any remote plasma formed outside the substrate processing region.

16. The method of claim 12 wherein the fluorine-containing precursor comprises a precursor selected from the group consisting of atomic fluorine, diatomic fluorine, nitrogen, trifluoride, hydrogen fluoride and xenon difluoride.

17. The method of claim 12 wherein the operation of flowing the fluorine-containing precursor into the remote plasma region further comprises flowing a hydrogen-containing precursor into the remote plasma region.

18. The method of claim 12 wherein the fluorine-containing precursor flowed through through-holes in a dual-zone showerhead and the nitrogen-and-hydrogen-containing precursor passes through separate zones in the dual-zone showerhead, wherein the separate zones open into the substrate processing region but not into the remote plasma region.

19. The method of claim 12 wherein a temperature of the patterned substrate is greater than or about 70° C. and less than or about 400° C. during the etching operation.

15

20. The method of claim **12** wherein a temperature of the patterned substrate is greater than or about 150° C. and less than or about 350° C. during the etching operation.

* * * * *

16

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 9,111,877 B2
APPLICATION NO. : 13/790668
DATED : August 18, 2015
INVENTOR(S) : Zhijun Chen et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

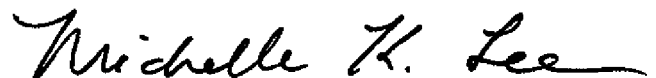
In the claims,

In column 13, line 53, delete “diluent” and insert -- effluents --, therefor.

In column 14, line 12, delete “duo” and insert -- into --, therefor.

In column 14, line 52, delete “nitrogen,” and insert -- nitrogen --, therefor.

Signed and Sealed this
Ninth Day of February, 2016

A handwritten signature in black ink, reading "Michelle K. Lee". The signature is written in a cursive style with a long, sweeping underline.

Michelle K. Lee
Director of the United States Patent and Trademark Office